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MECHANISM OF THE OXIDATION OF NICKEL AND CHROMIUM ALLOYS

By D. V. Ignatov and R. D. Shamgunova

Translated from the Russian version, published in Moscow in 1960.

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/Following is a translation of a Russian-language
book entitled "Mechanism of the Oxidation of Nickel
and Chromium Alloys" by D. V. Ignatov and R. D.
Shamgunova. The chief editor was N. V. Ageyev,
member-correspondent of the Academy of Sciences
USSR. The book was published in Moscow in 1960./

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INTRODUCTION

The extensive use of Ni-Cr alloys at high temperatures in oxidizing media is well known. Recently, nickel- and chromium-base alloys with additives of different elements have found extensive use in jet engine technology. The characteristic feature of these alloys is their sufficiently high heat-resistance in the temperature range of 950-1,050°.

However, works on the study of heat-resistant properties and, especially, on the investigation of the oxidation mechanism of Ni-Cr alloys have been published very little in Soviet literature.

Up to now the compositions of protective oxide films on even a simple, two-component 80% Ni-20% Cr alloy have not been established for the temperature range of 400-1,100°. E. Gulbransen and J. Hicman $/\overline{1}, 2/$ maintain that the protective film on this alloy consists of Cr_2O_3, and not $NiCr_2O_6$. K. Hauffe $/3, 4/$, on the contrary, considers that this film consists of a double oxide $NiCr_2O_4$ with the structure of spinel. O. Kubashevskiy $/\overline{5}/$, in comparing the results of works on the investigation of the oxidation of Ni-Cr alloys, writes that, from the articles mentioned, it is not yet quite clear exactly what determines good stability of Ni-Cr alloys against oxidation. The presence of Cr_2O_3 is an essential factor, but the stage in which this oxide must be formed, and whether or not its combining with nickel oxide in spinel form would be more protective, demands further study.

There is considerably less literary data on the oxidation of ternary and multi-component nickel- and chromium-base alloys.

Meanwhile, experimental data on the structure and properties of oxide films, formed on multi-component alloys in dependence upon temperature and heating time, are necessary not only for explaining the mechanism of chemical reactions and phase transformations in thin surface films, but also for developing methods of protecting metals and alloys from gaseous corrosion. These data also have important value in understanding the softening mechanism of heat-resistant alloys. As shown below, we have established the fact that the composition of oxide films on Ni-Cr alloys changes substantially, depending upon the time and temperature of heating these alloys, in which case the compositions of the oxide films do not correspond to that of the alloy. In this connection, both the chemical and the phase compositions of the alloys may change, which undoubtedly effects its mechanical properties.

In this monograph, the results of experimental studies of the oxidation mechanism of heat-resistant nickel- and chromium-base alloys, carried out by Soviet and foreign authors, are described.

Much of the text is devoted to the results of personal work by the authors in establishing kinetic laws for the oxidation of nickel-chromium alloys, in determining the structure, composition, and rate of growth of oxide films, and in studying the protective properties of these films which form on the alloys in dependence upon temperature and oxidation time, and upon aluminum, titanium, boron, and niobium additives.

For thoroughness, and in order to compare the heat-resistance of the alloys, the results of investigations of the oxidation of the base metals, nickel and chromium, are also given.

Principal methods of investigating the oxidation process of metals and alloys in gaseous media at increased and high temperatures (400-1,050°) are described in Chapter I.

In Chapter II, the main results of experimental works on the investigation of the oxidation kinetics, and on the structure and composition of oxide films (formed on Ni-Cr alloys and their individual components in dependence upon temperature and time of heating) are described.

Chapter III contains modern theories of the oxidation of metals and alloys, and reviews the possibility of using them to explain the oxidation mechanism of Ni-Cr alloys.

Chapter I

PRINCIPAL METHODS OF INVESTIGATION

1. Nature of the Oxidation Process

Before we describe the different methods, let us briefly review the essence of the oxidation process itself.

The experimental data available at this time on the oxidation process of metals and alloys show that this process is a complex crystallochemical and kinetic process which includes a number of other elementary processes. The first stage of the process is characterized by the direct reaction of the metal (or alloy) with an oxidizing agent (oxygen, sulfur, etc.) and, actually, is a case of chemical adsorption (more accurately, physical adsorption which quickly transforms into chemical). For all metals and alloys, this stage takes place very quickly, even at room temperature, and is completed after several minutes. Thereupon, oxide films are formed on the metal surface, their thickness being equal to the size of one or two elementary cells of the oxide /crystal/ lattice corresponding to the given metal. Since a metal-oxygen system is thermodynamically unstable (except gold) in a rather wide temperature range (including room temperature), the energy of activation of the oxidation process has little significance in this stage. An indirect verification of this hypothesis is the well-known fact of spontaneous combustion during rapid contact of thin films of many metals with oxygen, the films being prepared by vaporization and condensation /of the metals/ on unheated substrates in vacuo. This phenomenon is also exhibited by freshly recovered powders. The activation energy for the oxidation of beryllium at room temperature is 9 kcal/mole, and for molybdenum, 9.7 kcal/mole. Depending upon oxidation time, this stage is quantitatively expressed by an exponential law (with the exception of such metals as sodium and calcium, which, at room temperature, observe no law). With the formation of an oxide film 10-15 Å thick on the surface of a metal, the oxidation process takes place slowly and practically stops. For example, an oxide film of this thickness on aluminum forms after several minutes at room temperature, then, its further growth up to a thickness of 40-45 Å continues for 40-90 days.

The marked decrease in the rate of reaction between oxygen and the metal in this stage of the oxidation process may be explained by the fact that oxygen does not react with the metal directly, as in the first stage, because the reagents, metal and oxygen, are separated by an oxide film.

Atoms (or ions) of the metal and oxygen must now pass through an oxide film in order to come into contact and react with each other. For this purpose, they must possess sufficient kinetic energy to overcome the bond energy between the ions of the metal

and the oxygen of the oxide lattice which is formed in the first
oxidation stage as a result of the change in the free energy of
the metal-oxygen system. Such a reserve of energy at room tem-
perature, according to Boltzmann's famous law of distribution, is
possessed by only a small number of the atoms of a system. There-
fore, the oxidation process of this new, or 'secondary," stage
takes place slowly, and practically stops when a rather thick
oxide film forms on the metal surface. Such films are called
limiting films. For the majority of metals, they have a thickness
of 50 Å at room temperature, and are protective against oxidation
up to 200-300°, in which case their thickness increases to 100-
200 Å. Hence, without supplementary activation energy, the oxi-
dation process does not take place of itself in the second stage.

It is known that the oxidation process is comparatively
easy to activate by heating the whole system, or by activation of
an oxidizing medium. In the first case, the metal and the oxide
phase are activated, mainly, because, as the temperature increases,
the bonding forces between the atoms or ions in the lattices of the
solid phases become weaker, and the coefficient of the diffusion of
metal and oxygen through the oxide film increases. In the second
case, mainly gaseous components are activated, for example, oxygen
may be activated by an electric discharge, or by irradiation with
an electron beam, α-particles, etc. As a result of these actions
on oxygen, active particles are created: ions (O^-, O_2^-, O_2^+, O^+),
atoms, and excited atoms and molecules. With the aid of a glow
discharge, as shown in works $/6$, 9-$12/$, some metals (particularly
noble metals) are intensively oxidized in activated oxygen at 40-
100°. For example, aluminum films 400 Å thick are completely oxi-
dized at the anode of a discharge tube in a glowing (oxygen) dis-
charge after 30-40 minutes at a current density of 1-2 ma/cm². A
silver film of the same thickness would be completely oxidized
after a few seconds $/13/$.

However, heating metals and alloys, especially at elevated
and high temperatures, leads to a higher rate of oxidation than
the activation of oxygen by irradiation or discharge (with the
exception of noble metals). The rate of metal oxidation upon heat-
ing will be determined by the following factors: crystallochemical
relationship between the metal and oxide lattices; parameters of
the diffusion of metal or oxygen ions through the oxide film, de-
pending upon the types of defects in the $/$crystal$/$ lattices of the
oxides; phase and chemical transformations in the film (especially
in multi-component oxide films); and phase and other transforma-
tions in the metal itself.

Other factors also affect the rate of oxidation, such as:
stresses arising in the scale $/$film$/$;
recrystallization processes in the film;
the development of grains;

and the physicochemical properties of the oxides (stability, volatility of the oxides, melting point, coefficient of expansion, porosity, plasticity, and mutual solubility /miscibility/ of metal and oxide).

In the case of alloys (especially multi-component alloys), to those factors which affect the oxidation rate may be added the following:

1) thermodynamic activity of alloy components, which will be determined by the concentration of ions of the different components at the alloy-film boundary;

2) parameters of the diffusion of these components through the film;

3) secondary oxidation and reduction reactions in the film at the alloy-film boundary;

4) reactions between oxides of the different components in the film, of the type: $NiO + TiO_2 = NiTiO_3$; $NiO + Al_2O_3 = NiAl_2O_4$, etc.; and

5) decomposition of complex oxide compounds at high temperatures, and vaporization of some of them.

From this review of the oxidation process, it is apparent that this process is conditioned by many factors, even in the simplest case when the samples are not under conditions of simple or cyclic heating, and are also not subjected to heating at various frequencies of heat transfer and in various corrosive gaseous media. Therefore, to broaden and intensify investigations of the oxidation process, both in general and in order to study the mechanism of the interaction of metals and gases, it is necessary to use several methods of physicochemical analysis.

Since the measure of the intensity of an oxidation process is its rate, and the ultimate goal of investigating this process is to work out methods and proposals for protecting metal and alloy articles from the corrosive attack of gases, among the main methods of investigation will be kinetic methods. To these methods, first of all, belong gravimetric methods, by which the rate of oxidation is determined by the change in weight of the sample (in $g/m^2 \cdot$ sec, or actually, $mg/cm^2 \cdot$ hr), depending upon the time and temperature of heating the sample, the concentration of alloying additives in the sample, and upon the nature of its treatment before oxidation (melting, forging, tempering, etc.).

By these experimental data, expressed as curves whose coordinates show increases in weight (in mg/cm^2) as functions of time (in hours or minutes), or in analytical form as equations which correspond to these curves, it is possible to establish laws of oxidation and, in accordance with these laws, determine the constant (k) of an oxidation reaction.

The oxidation process in the temperature interval from 20° to near melting point, for most metals, takes place according to

the following time rules (i.e., the dependence of the increase or loss of weight Δm upon time t): As an exponential or logarithmic function, $\Delta m = k \lg (at + 1)$ at low temperatures; as a cubic function $(\Delta m)3 = kt + c$ and a parabolic function $(\Delta m)^2 = kt + c$ for medium and higher temperatures, and as a linear function $(\Delta m)^2 = kt + c$ /sic!/ /See note/ at high temperatures.

(Note: The errata corrects Δm^2 to Δm.)

The constant c in the last three equations only determines the presence of an oxide film on the metal surface when the time $t = 0$, for example, the formation of an oxide film during the mechanical (polishing) or chemical (electropolishing) treatment of the surface of a sample. The thickness of this primary oxide film is low (not over 100 $\overset{o}{A}$), and may therefore be disregarded in determining the rate of high temperature oxidation. This constant is the basic parameter of the oxidation process.

In most cases, as the results of experimental investigations of metal oxidation processes have shown, the rate constant, depending upon the temperature of oxidation, is expressed by Arrhenius's equation:

$$k = Ae^{-Q/RT},$$

where A is a constant whose rate is determined by the rate of k; and Q is the activation energy of the oxidation reaction.

From this equation it follows that log k, depending upon $1/T$, is a linear function. Therefore, in plotting a graph based on experimental values of k with coordinates of log k $1/T$, it is possible to determine the activation energy (Q) of the oxidation process from the tangent of the angle of inclination /i.e., the slope/ of a line.

The activation energy is the second main energy parameter, which characterizes an oxidation reaction from a quantitative point of view (i.e., determines the strength of bonding forces in the lattices of the oxide and metal).

By comparing the values of rate constants and activation energies for different metals in a comparable temperature interval, it is possible to evaluate the oxidizability of these metals at these or any temperatures, and their (the metals) suitability from practical use.

If the experimental data substantially deviate from some law of oxidation, then for the characteristics of the intensity of the oxidation process, the mean oxidation rate for a given time interval at a given temperature may be determined gravimetrically.

Data on rate constants and activation energies of the oxidation process of metals may be obtained manometrically by measuring the pressure of the oxygen in a reaction vessel after the absorption of oxygen by the oxidized metal. An essential deficiency of

both methods is that, in determining the oxidation rate, it is
necessary to know the true surface area of the sample, which is
measured during the process. Therefore, actual increases in
weight refer to the visible area, although a correction is some-
times introduced to compensate for roughness /of the surface/ by
multiplying the geometrical area by the coefficient of roughness.
The coefficient of roughness is the relationship of the size of
the true surface to the size of the geometrical surface area of
the sample.

The true surface area is determined by special tests with
the adsorption of argon (or some other inert gas) at the tempera-
ture of liquid oxygen /14/.

For a polished surface this coefficient equals ~2, but for
thin metal films, deposited by vaporization and condensation in
vacuo, it may change from 2 to 20 or more, depending upon the melt-
ing point of the metal and its speed of vaporization. According
to data obtained by electron microscopy and electronography, the
size of crystals in thin films of easily melting metals such as
magnesium and aluminum is 200-300 Å, but for titanium and chromium,
~ 20-30 Å, i.e., twenty times less. Probably, the relationship of
the roughness of metal films condensed on a cold substrate will be
of this same order of magnitude. The coefficients of surface
roughness of pickled samples or surfaces, produced by reduction
of the oxides with hydrogen, have values of 20-1,000, depending
upon the methods of pickling and reduction /15/.

However, during high-temperature oxidation the initial sur-
face roughness disappears after the first few hours of oxidation,
and all the faster as the temperature increases. Thus, for exam-
ple, according to our data, the effect of the surface roughness
of samples of a nichrome alloy, created by polishing with emery
paper 4/0, disappeared after 5 hours heating at 600°, and after
2-3 hours heating at 800-900°. Hence, for long periods of oxida-
tion, 25-30 hours, for example, the influence of the initial sur-
face roughness on the oxidation rate may be disregarded. The
change in the degrees of roughness during the oxidation process
is one of the reasons for the high oxidation rate observed during
the first part of the process, and the decrease in this rate during
the latter part.

Sometimes several other methods are used, by which the oxi-
dation rate is determined by the thickness of oxide (or other)
films growing on the surface of metallic samples in dependence
upon temperature and heating time. Some of these methods are: op-
tical, according to change in color (interference); polarization,
according to change in ellipticity and the change in the initial
intensity of light due to thickness /of the film/, as a result of
absorption; electrical, according to the change in electroconduc-
tivity; and electrochemical, according to the reduction of oxides.

As we have pointed out, by kinetic methods it is possible to determine two basic parameters of the oxidation process: the rate constant, or mean rate, of oxidation, and the activation energy of the process. However, it is not possible to explain the oxidation mechanism of metals and alloys and to solve the problem of protecting them from gaseous corrosion on the basis of data on these parameters alone. Without analysis of the reaction products and data on their physicochemical nature, the kinetic laws themselves and the dependence of the values of rate constants and activation energies on temperature and the composition of the alloys cannot be explained. Therefore, alongside, and in close connection with kinetic methods, it is necessary to use analytical methods, which include the following: methods of chemical analysis; structural methods (radiography, electronography, neutronography, metallography, and electron microscopy); and isotopic methods (methods employing radioactive and stable isotopes).

As to supplementary methods which allow the determination of physicochemical properties of metallic and oxide systems, and mainly, the bonding energy of their /crystal/ lattices (if these data are not available), one might point out the thermographic and calorimetric methods, and methods for determining the energy of sublimation and thermodynamic activities, and also the nature of conductivity (the determination of Hall's coefficient) and the coefficients of thermal expansion.

This monograph briefly reviews the use of the gravimetric method, structural methods (besides radiography and neutronography), and isotopic methods of investigating the oxidation process of metals and alloys. Other methods are described in works /5, 16-18/.

2. The Gravimetric Method

The gravimetric methods facilitate the determination of the oxidation rate at a given temperature either by increase in weight or by loss of weight from a sample (in the case of volatile oxides or in an instance of working parts), in unit time or per unit area of the geometrical surface of a sample. The increases in sample weight themselves may be determined either by periodic weighing or continuous weighing after initiation of the oxidation process.

Methods of determining the oxidation rate of samples by loss in weight, and also, the results of investigations of gaseous corrosion in different gaseous media and under conditions of cyclic heating, are described in works 5, 18-20, and therefore, will not be discussed here.

Increases in the weight of samples due to oxidation, with both periodic and constant weighing, is determined, in the majority of cases, on standard microanalytical scales with a sensitivity of $2 \cdot 10^{-5}$ g according to the graduation of the optical scale of a reading microscope.

The samples and their treatment before oxidation were the same in both cases. The samples, actually, must at the time of testing be in the same crucible, tempered to a constant weight at a temperature which exceeds the highest test temperature by 150-200°. In choosing crucibles, one should consider the possible interaction of the crucible material with the oxides formed on the surface of the sample, as a result of which, the oxidation rates of samples in crucibles of different materials, and under widely differing conditions, may prove to be unalike. Only in those cases where it is certain that the oxide films are not peeling or crumbling from the sample should crucibles be dispensed with in heating the samples.

Each method of periodic and continuous weighing has its advantages and disadvantages. In periodic heating, several samples (20-25) may be loaded into the furnace at one time, which is an important condition for obtained average values for weight increases but also for studying oxidation mechanism jointly with other methods (for example, structural methods).

This method allows more accurate determination of the surface temperature of the sample by permitting direct contact between the head of the thermocouple and the sample, and allows more accurate determination of weight increases than in the case of constant weighing.

A substantial disadvantage of the method is that, upon alternate heating and cooling, in some cases the film (or coating) partially or completely peels from the sample due to mechanical shearing stresses. This stress is created in the coating as a result of different coefficients of thermal expansion of the metal and the oxide, and also, the difference in the volume of a metal and its corresponding oxide. After each heating and before weighing, the sample in the crucibles should be cooled and kept in an exsiccator with calcium chloride or some other water vapor absorber.

The weighing operations are especially complicated if the oxidation tests are carried out in pure oxygen.

During the entire test of oxidation in a gas (oxygen), the samples are not removed from the reaction tubes or the electric furnace when the continuous weighing technique is used. Periodic change of weight over a determined time interval is computed according to the scale of a measuring microscope or registered with a photoelectric transmitter and an electronic potentiometer.

The main difficulty in weighing in this case is that it is hard to overcome the vertical and horizontal stresses resulting from the transfer of air (or oxygen), and also, avoid vibrations of the walls and floor, which arise from the operation of compressors and pumps, and even from the movement of city traffic.

It is expedient to make the apparatus hermetic during the continuous weighing operation, which allows experiments on oxidation to be carried out in pure oxygen or some other given composition

of gaseous oxidizing medium. The peeling off of an oxide film from a sample is also possible in the given case as a result of the crystallochemical transformation of the /crystal/ lattice of the metal into that of the oxide. These stresses are especially great when the volume of the oxidized metal is 1.5-3 times less than that of the corresponding oxide.

The factor of alternate heating and cooling, which leads to cracking and peeling of the coating, has no effect on the oxidation rate when the continuous weighing technique is used.

However, one should bear in mind that under actual conditions articles made of metals and alloys are used under cyclic temperature conditions. Therefore, in evaluating the corrosion stability of a material, the results cannot be based solely on data on the oxidation rates obtained by the continuous weighing method.

In explaining the oxidation mechanism, those factors which affect the reaction rate, for example, peeling of the oxide film during alternate heating and cooling, should be considered. By applying both of these methods to the same object, more complete and reliable data on the oxidizability of the material may be obtained.

Since the periodic weighing method permits joint experimentation in the oxidation of metals with many objects, then it is possible to also select a number of samples when the periodic and continuous oxidation processes are to be combined.

For this purpose, and to study the structure and composition of a coating, 22 samples must be prepared which are entirely similar in composition and in the degree of surface roughness. Then, based on an estimation that, with the length of the experiment being 25 or 50 hours, eight points must be obtained for plotting a curve of oxidation kinetics with coordinates in terms of increase-in-weight and time, at set time intervals, 5 samples may be taken out and weighed. Three of these (same samples) will be heated and cooled alternately during the test period, while the remaining two, on the other hand, will begin anew after each consecutive period of heating.

In this way, for each point of the kinetic curve there will be five increase-in-weight values, three for samples subjected to periodic oxidation and two for those subjected to continuous oxidation. The latter two samples are subsequently used for electronographic phase analysis of the coating, and for electron-microscopic and metallographic studies of their microstructure. The coating of these samples may also be used for analysis of their chemical composition. Three of the 22 samples would be oxidized continuously for 25 or 50 hours. Then their coatings would be subjected to thorough investigation. In order to construct a graph of log k - 1/T and determine the activation energy values, the rate constant for

four different temperatures (in a comparatively small temperature interval) must be determined. Consequently, 84 samples in all are needed for complete kinetic and structural investigation at four heating temperatures.

This over-all method of studying the oxidation process, in contrast to the other partial methods reviewed above, will henceforth be called the structural-kinetic method. A special feature of the stated method is that it gives the possibility of obtaining data on average oxidation rates, phase and chemical compositions of the film, and also, on the microstructure of the film for all points on the experimental curve of oxidation kinetics.

3. The Electronographic /Electron Diffraction Pattern/ Method

The basis of the electronographic method is the investigation of the diffraction of electrons due to the coherent scattering of an electron beam (20-500 microns in diameter) by the crystal lattice of a substance when the beam is passed through thin films of the substance. By a given substance, an electron beam is scattered 10^4 times more intensively than x-rays. Therefore, the electronographic method is foremost among the structural analytical methods in investigating the crystal structure and composition of oxides in surface films formed on metals and oxides during their interaction with and oxidizing medium in dependence upon temperature and heating time. The method also allows the determination of crystallochemical and phase transformations in thin free films of various substances (without substrates) with thicknesses up to 1,000 Å and in surface layers with thickness from 20 Å.

Soon after the first experiments by Germer and Davisson in 1927 on the diffraction of electrons, the electronographic method began to be used in studying the structure of oxide films. Thus, in 1930-1934 /21-23/, the first determinations were carried out on the structure and composition of oxide films on copper, iron, and nickel, their thickness being ~ 100 Å. In this way, the prediction of Academician V. A. Kistyakovskiy (1909) /24/ was verified, which supposed the formation of invisible, thin films on metals at room temperature in air, the films consisting of oxide phases (and not of adsorbed layers of oxygen, as assumed by J. Langmeier), in colloidal state, and transforming from this state into the crystalline state as their thickness increased /25/.

Study of the oxidation mechanism of metals and alloys by the electronographic method (along with other methods) have been carried out in the Soviet Union from 1934 through 1952 mainly under the leadership of P. D. Dankov, and were centered at the Institute for Physical Chemistry of the USSR Academy of Sciences.

At present the electron diffraction method is widely used in different branches of science and technology by many of the institutes and research establishments of our country.

In this book, only the use of this method for qualitative analysis of the phase composition of films on metals and alloys will be described. The theory of electron scattering and the principles of structural electronographic analysis, and also, the different fields of application of the electronographic method are described in a number of monograph and review articles /26-32/.

With the aid of electronographic analysis, the atomic structure of the oxide contained in the oxide film on the surface of oxidized samples is determined. By carrying out this analysis jointly with determining the oxidation rates, data may be obtained on the laws of the formation of oxide phases and their transformations, depending upon the composition of the alloys and the oxidizing medium, and the temperature and heating time; and it is also possible to determine the phase and chemical compositions of oxide films on samples of some alloy or the other. Herein is included the main problem of using the electronographic method to study the oxidation processes of metals and alloys or processes of the interaction between metals a gaseous or liquid media in general. Although the electronographic analysis of the phase composition of film is, in this case, mainly qualitative, it is nonetheless important in solving the stated problem.

The possibility of successfully using the electronographic method for quantitative phase analysis was recently shown by L. S. Palatnik and B. T. Boyko /33, 34/ in studying the decomposition process of a supersaturated solid solution in thin films of aluminum- and nickel-base alloys. These authors originally and successfully solved the problem of superimposing two distorted electronograms /electron diffraction patterns/ on the same photographic plate from two standard samples (for example, from Al and $CuAl_2$ in the system Cu-Al).

The electronograms, distorted and superimposed upon each other, were obtained by periodically shifting the primary electron beam from one side to the other with deflection plates (located between the electron source and the object), to which were supplied electromagnetic current impulses of rectangular form. By setting up a set impulse length or frequency, it was possible to obtain superimposed electronograms with the necessary relationship between the intensity of the lines being compared on fundamental and distorted electronograms. According to the data of these authors, the impulses were supplied with a frequency of 10 kc, which, with an exposure of 1-2 seconds, completely assured analogous conditions for obtaining electronograms from both of the standard samples.

The relationship of the volume concentrations of the phases in an alloy were determined by comparing the intensities of lines on a standard superimposed electronogram and those on an electronogram from the two-phase alloy Al + $CuAl_2$. In comparing data from

the electronographic phase analysis with data computed after a method by S. A. Vekshinskiy, the authors found that these data correspond with an accuracy of 2-3%.

In principle, this method of obtaining superimposed electronograms may be used also for bulk samples if there phases are not distributed in layers. In thin films, the phases in a heterogeneous alloys may also be distributed in layers. This fact should always be kept in mind during phase analysis.

It is necessary also to see to it that the thickness of the film and the dimensions of the crystals in them are the same for both the standard and the investigated samples. In both cases, the electron-microscopic method of studying the secondary (crystallite) structure of objects must be used.

The technique of qualitative electronographic phase analysis of films itself is quite simple if electronograms with sharp diffraction lines are obtained from the samples, and if the film itself consists of oxides with known structures. The first stage of analysis consists in determining the instrument constant λL from the formula

$$2 \lambda L = dD,$$

where D is the diameter of the diffraction ring in millimeters; d is the value, with respect to this ring, of the interarea distance from the standard sample in Angström units; L is the distance from the object to the photographic plate; and λ is the wave length of the electrons.

Very often, one of the phases of a given sample may serve as the standard /control/ substance. For example, a gradually oxidized metal may be chosen as a standard during the oxidation of thin films of metals or their solid solutions. Then the value of the instrument constant λL is determined according to the given formula as an average over three strong lines of the metal, in which case preference must be given to lines of large diameter. For rings of large diameter, the relative error $\Delta D/D$ in measuring their diameters will be less than that of lines of small diameter. Actually, it is recommended that diffraction rings with diameters of 30-50 mm be chosen for determining the instrument constant on an electronogram. Then, upon measuring the diameter of a ring with an accuracy up to 0.1 mm the relative error will be about 0.2-0.3%.

If the phase composition of a coating is determined on samples in the form of thin films deposited from aqueous (or other) suspensions onto a substrate, usually of and amorphous organic substance, as, for example, cellulose or collodion, table salt is used as a standard substance, for the most part, being introduced into the aqueous suspension in the amount of 0.1-0.05%.

Thin metal films may also be used as standards, the former acting as substrates at the same time. For this purpose, thin

aluminum films are widely used in our practice, the films being obtained by vaporization and condensation in vacuo; and their electronograms contain sufficiently sharp lines by which the instrument constant may be determined with complete accuracy.

It is considerably more difficult to determine the instrument constant from electronograms obtained from bulk samples by the refraction method because it is very difficult to obtain a diffraction pattern of the standard and the investigated surface of a sample simultaneously on the same photographic plate.

Therefore, it is most often the practice to determine the instrument constant by taking the electronogram of the sample for a short period of time (a second or less) after obtaining electronograms by reflection, in which case, both electronograms may be received either on the same photographic plate or on different ones. With good stabilization of the high voltage (about 0.01-0.03%), such a method of determining the constant is quite reliable.

Besides this method, since 1952 we have been using a method (proposed by D. V. Ignatov) of simultaneously obtaining the electronogram of the test sample by the reflection method and obtaining that of the standard (aluminum films) by the penetration method, on a single photographic plate. For these purposes, a thin aluminum film, deposited on a screen, is placed at the lower edge of the sample so that the screen with the film rises a little (approximately 1 mm) above the test surface of the bulk sample (Figure 1). Figure 2 shows two electronograms obtained simultaneously by reflection from the surface of an oxide film, consisting of $NiCr_2O_4$, and by penetration of aluminum films.

The second stage of phase analysis consists in measuring the diameters of the diffraction rings on electronograms of samples in the form of thin films and layers, or in measuring the radii of these rings on electronograms of bulk samples, obtained by the reflection method.

The diameters and radii are measured either with a standard ruler (preferably graduated in 0.5 mm units), with an accuracy of up to 0.1-0.2 mm, or with a comparator, with accuracy up to 0.01 mm. The center of the diffraction rings on electronograms (obtained by /electron/ penetration) is the trace of the central electron beam which appears as a hole in the photographic emulsion or a dark spot.

When studying such a trace by the reflection method, it sometimes corresponds to the true geometrical center of the half-rings on the electronogram and sometimes, not at all. To find the center in such cases, it is helpful to use celluloid sheets onto which 2-3 of the half-rings may be transferred /traced/ and determine the center according to them, but not by the lines on the electronogram itself, in order to avoid damaging it. The center

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of a diffraction pattern may be determined in the reflection technique with stencils of the rings or half-rings transferred onto the celluloid sheets with radii /of the rings/ computed for different values of the interarea distance d with a known value of the instrument constant, i.e., according to the formula $D = 2\lambda L/d$. By laying the constructed diffraction pattern on the electronogram of some sample in this manner, the center of the half-rings on the electronogram may be determined by superposing 2-3 of the /transferred/ rings on them.

The interarea distances d which correspond to the values of the diameters or radii are computed according to the formula

$$\frac{d}{n} = \frac{2\lambda L}{D} \text{ or } \frac{d}{n} = \frac{\lambda L}{R},$$

where L, D and R are measured in millimeters, and λ, in Angström units.

In more accurate evaluations of electronograms, the values of d are computed according to the equation:

$$\frac{d}{n} = \lambda \frac{L}{R} \left[1 + \frac{3}{8}\left(\frac{R}{L}\right)^2 - \frac{13}{128}\left(\frac{R}{L}\right)^4 + \frac{55}{1,024}\left(\frac{R}{L}\right)^6 - \ldots \right] \tag{1}$$

The third stage is the determination of the intensity of diffraction lines. In determining structure or in carrying out quantitative phase analysis, intensities are determined, just as in x-ray analysis, by microphotograms obtained with the aid of graphic microphotometers. The photometric method of determining intensities is similarly described in /35, 27/. In qualitative analysis, for the most part, a visual evaluation of the relative intensity of lines, according to a nine-point scale, is sufficient. In a nine-point scale there are three points (very, very strong -- VVS; very strong -- VS; and strong -- S) which refer to strong lines; three which refer to lines of medium intensity (medium strong -- med S; medium -- med; and medium weak -- med W); and three which refer to lines of weak intensity (weak -- W; very weak -- VW; and very, very weak -- VVW).

In evaluation intensities, the uneven distribution of the intensity of the background on the electronograms should always be considered, especially when using substrates of the celluloid type. In many cases, on reflection electronograms of bulk samples, such a strong background is observed in the region of the central spot (sometimes extending to a distance up to 15 mm from it), that several diffraction rings will fall in this region and will not be noticed at all or will have weak intensity. Therefore, in order to obtain more diffraction rings on the electronogram, less exposure must be used for the central part of the diffraction pattern

than for the periphery, and both of these parts must be photographed separately.

The method of multiple exposures, usually used to evaluate the intensity of lines on electronograms of samples in the penetration method /i.e., passing the electron beam through the test sample/, may also be used for electronograms in using the reflection technique. Accurate and direct determination of absolute intensity values is possible with the aid of counters and photoelectric multipliers, using an attachment to take away the background. The method of recording diffraction patterns, propounded recently /37/, given the possibility of solving this problem. The electrometric method of recording considerably simplifies and increases the accuracy of quantitative and qualitative electronographic phase analysis.

Qualitative analysis concludes with comparing the values of the interarea distances, computed from electronograms of the oxide film, with those values (tabular) obtained for a prospective oxide (or combination of oxides) by the radiographic (x-ray) method. If, during this comparison, it seems that the values for three (or more) of the basic and characteristic lines with the strongest intensity on the electronogram of the oxide correspond to the tabular values of the interarea distances with sufficient accuracy (0.3-0.5% for penetration electronograms and 0.8-1% for reflection electronograms) for lines of the same intensity, then the oxide (or other) phase in the coating of a sample is considered to be established. The problem of establishing the oxide phase in the oxide film of a given sample is considerably simplified by the fact that its chemical composition is usually known earlier, and the fact that the structure (based on x-ray data) and the thermodynamic characteristics (heats of formation, melting points, stability, etc.) of oxides of the different alloy components are known. However, the possibility of the formation of oxides with new and unknown structure, or with a structure where the parameters of the /crystal/ lattice deviate considerably from those of a prospective oxide or oxide compound, is not excluded. In such cases, to determine the crystal structure and establish the nature of the phase on this basis, all the means of electronography and radiography are utilized, and in some cases, neutronographic analysis. Regardless of the very high absolute sensitivity of the electronographic method of investigation (it is possible to obtain a diffraction pattern from a substance in the amount of 10^{-12} g), its accuracy in determining the phase composition of mixtures of oxides and of other compounds does not surpass the accuracy of the x-ray method, and is equal to 1-5%.

Besides phase analysis of a coating, the electronographic method may be successfully used to determine the orientation of the crystals in an oxide film with respect to the metal crystals at the surface of a sample.

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In a detailed study of the orientational relationship between the crystals of an oxide film (or the new crystal phase in general) and the lower-lying metal layer or the crystals in the surface layer of the substrate in general, upon which the new phase grows, P. D. Dankov established the principle of "orientational and dimensional homology" /38/. On the basis of this principle, P. D. Dankov /39, 40/ and V. I. Arkharov /17/ created the bases of the crystallochemical theory of the oxidation of metals and alloys, which will be discussed below. Many of the works of V. I. Arkharov and his co-workers /41/ are devoted to the investigation of types and the natures of different textures in a coating, and to the kinetics and oxidation mechanism connected with them. A number of works in this field have been carried out by N. A. Shishakov /42/.

4. The Electron Microscope Method

The electron microscope method of investigation and the related apparatus are widely described in a number of monographs and review articles /43-45/. Therefore, these problems will not be discussed here. We shall only briefly discuss the fundamental problems of investigating oxidation processes, which may be successfully solved with the aid of the electron microscope. The following may be included in problems of this nature: Investigation of the formation and growth of oxide crystals on different facets of the metal grain; Study of recrystallization processes in oxide films, depending upon time and temperature of oxidation; Determination of microscopic fissures and pores in oxide films; and, Investigation of chemical and phase transformations in thin free films (i.e., without substrates) of metals, alloys, and oxides.

The first three problems are solved by the "replica" method, and the last, by x-ray analysis of films with thickness nearly equal to the size of the crystals in the film.

The methods and results of investigations of the mechanism of the formation and growth of primary crystals (nuclei) of oxides on different areas of some metal crystals are described in works /46-48/.

Recrystallization processes in oxide films on metals and alloys in dependence upon temperature and heating time were studied by D. V. Ignatov and co-workers. Microphotographs were obtained with the aid of both lacquer (emulsoid) and quartz or coal replicas. It should be mentioned that all replicas are obtained from the oxide surfaces of films without any chemical or mechanical treatment of the surface of the sample. Therefore, the replicas transfer the true relief of the oxide film, and the size and shape of the crystals in the film, just as they are created as a result of the oxidation process alone. The size of crystals increases both with the

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increase of temperature and with prolonged heating time in limits
of from 20-30 Å at 20-100° up to 10^4 Å at 1,000-1,200°. The re-
crystallization process considerably increases and begins at lower
temperatures in those cases where the volume of the oxide is 2-3
times greater than that of the oxidized metal (for example, iron,
chromium, and molybdenum), although in thin free films (without
substrate) of oxides of these metals, similar intensity of the re-
crystallization process is not observed. This effect of accele-
rated recrystallization of the oxide films of the stated metals
may be explained by the high compression stress in the coatings.
Upon investigating the oxidation kinetics of multi-component al-
loys, it may be observed in some cases that the phase composition,
according to electron microscope data, does not change; but the
oxidation rate, determined by increase-in-weight, after a short
time. The authors have observed similar sharp changes in the oxi-
dation rate of alloys with additions of boron at temperatures over
1,000° in dependence upon time. With the aid of the electron micro-
scope 200-500 Å pores have been discovered in the coating on sam-
ples of such an alloy (see figures 26-29).

The electron microscope permits the study of interaction
processes of metals with oxygen and the growth of oxide crystals
in dependence upon temperature and heating time by x-ray analysis
of thin metal films prepared by condensing vapors of the metals
in vacuo at 20-80°. However, we must point out that the use of the
electron microscope method of studying such processes in thin films
is limited, because, in such cases, when the thickness of the films
is several times larger than the size of its crystals, electron
microscopes show distorted images because of the superposition of
the image of one crystal upon that of the other. Only when the
thickness of a film is equal to the average size of its crystals
is it possible to trace the change in their shape and dimensions
during the recrystallization and oxidation processes. Along with
this method, the metallographic method may be successfully used to
discover intercrystalline corrosion, pores and fissures in the
coating, and also, for studying the cross sectional structure of
the coating.

5. The Isotope Method

Since the oxidation processes is accomplished by means of
the diffusion of reacting elements (metal ions and oxygen), the use
of isotopes in studying the oxidation mechanism may be useful and
very important. For these investigations, radioactive isotopes of
the metals and the stable isotope O_3^{16} are used. As in ordinary

diffusion studies, the parameters of the diffusion of a metal or
oxygen through its (the metal) oxide and the temperature dependency

of the diffusion coefficient are determined with the aid of the above-mentioned isotopes. By comparing the values of the coefficients of the diffusion of the metal and oxygen ions through the oxide of a given metal, it is possible to establish how the oxidation process takes place due to the diffusion of such ions. As, for example, in determining the diffusion parameters of ions of copper and oxygen through the oxide Cu_2O at $1,030°$ $/49/$, it was established that the diffusion coefficient of oxygen at a pressure of 135 mm Hg was $1.3 \cdot 10^{-9}$ cm^2/sec, and the diffusion coefficient of copper was $4.8 \cdot 10^{-8}$ cm^2/sec. From a comparison of the values of these coefficients, it follows that, in the oxidation of copper, the diffusion of oxygen is less than that of copper.

Coefficients of the diffusion of oxygen in oxide systems are found by the K. Zimens method $/50/$ of determining the rate of exchange between the oxygen of the oxide and gaseous oxygen enriched with isotope O^{18}. This method of rate determination in dependence upon temperature is described in detail by Ye. I. Dontsova $/51/$. Methods of determining the parameters of the diffusion of a metal in oxides is described in works $/52-54/$. Unfortunately, it is difficult to compare the rate constants and activation energies of the diffusion of these same metals, or oxygen, through their oxides because metal oxidation processes are usually studied at lower temperatures than those at which diffusion processes are studied. For example, the oxidizability of aluminum is studied at $20-600°$, that of cobalt, nickel and chromium, at $20-1,000°$, and that of titanium, zirconium, and niobium, at $20-900°$.

Diffusion processes of the metals in oxide systems take place at a measureable rate at $1,100-1,400°$. At temperatures up to $1,100°$, the boundary diffusion of samples prepared by sintering is so intense that an accurate determination of the true parameters of the volume diffusion of the metals in such samples is not feasible. One should also remember that during diffusional tempering at high temperatures $(1,100-1,400°)$, many metals and some oxides $(ZnO, NiO, Cr_2O_3,$ and others) are intensively vaporized, and an active metal layer, deposited on the samples from the oxides, is oxidized by the oxygen which remains in, and is separated from, the walls of the ampule. During tempering in quartz ampules evacuated to 10^{-5} mm Hg at $1,100-1,200°$, marked vaporization of SiO_2 from the walls of the ampule and diffusion of oxygen through these walls are observed, which phenomena were discovered by D. V. Ignatov and V. V. Votinova by special experiments. Along with the test samples, control samples in the shape of thin chromium and aluminum films (300-400 Å thick) were placed in quartz ampules, the films being set upon platinum racks. After diffusional tempering, the electronographic method was used to determine which aluminum film had been completely oxidized, in which case, the compound $SiAl_2O_5$ was formed. The chromium film was vaporized completely (probably after oxidation).

The effects of vaporization and oxidation are somewhat less-ened when the ampule is filled with pure argon to a pressure of 200 mm Hg and pure zirconium (iodide) is placed in the ampule. Diffu-sional tempering at $1,100-1,400°$ must be carried out in ampules poured from pure aluminum oxide ($\alpha = Al_2O_3$) or beryllium.

These temperings may also be carried out in microfurnaces introduced into evacuated (or argon-filled) molybdenum glass tubes cooled by water.

More accurate data on the parameters of diffusion in oxide systems may be obtained on fused samples by using iridium crucibles to melt the oxides. Boron carbide discs are recommended for re-moving active layers from the oxide samples. These discs, 15-20 mm in diameter and 2-3 mm thick, are pressed from fine boron carbide powder (with water or alcohol added) and annealed in a furnace at $600-700°$ in air. Active layers of the given thickness may be re-moved more accurately by using a (biological) microtome with the steel knife replaced by a plastic one with the boron carbide discs mounted on it.

Study of the diffusion processes of metals in oxide systems at high temperatures has important significance not only for study-ing the oxidation mechanisms of metals, but also for explaining the mechanism of the destruction of oxide refractories upon interacting with metals.

6. Samples /of Metals and Alloys/ and Their Processing Methods

Samples in the form of 15 x 10 x 5 mm sheets are used as standard samples for studying the oxidation processes of metals, and especially alloys, with the aid of the structural-kinetic method described in Section 2.

The latter dimension -- the thickness -- may be 3-4 mm. Such samples are satisfactory for both kinetic and electronographic studies.

Thin films of metals and alloys, obtained by vaporization and condensation of metals in vacuo, although not basic, are ex-tremely important for studying the oxidation mechanism of metals and alloys. Thin films model in some degree the chemical composi-tion of bulk samples, and are the standards. With the aid of these samples, the temperature intervals for the formation and decomposi-tion of different phases in alloys and oxide systems may be deter-mined in a short time. Moreover, thin metal films may be used for precision studies of the primary stages of oxidation (adsorption, dissolving, and formation of oxide phases) at low and medium tem-peratures ($100-500°$), employing manometric and microgravimetric methods. Samples of 0.05-0.3 mm thick tin foil may be used for this purpose. Whenever thin films or samples prepared from tin

foil are used, both fronts of the reaction (or the boundaries of oxygen dissolving), which move from the outer boundaries of two sides of the sample to its central inner boundary, must not meet during the oxidation of sheet-like samples; and during the oxidation of thin metallic films, the reaction front (or boundary of oxygen dissolving) must not reach the surface of the substrate upon which the films are located.

If these precautions are not observed, then the kinetic curves in terms of coordinates of increase-in-weight and time will be asymptotic, and erroneous conclusions as to the oxidizability of a given metal or alloy may be given on the basis of these curves. The nature of the processing given the surface of samples prior to oxidation is also very important in the study of oxidation kinetics. Standard laboratory practices include the following processing techniques; and mechanical buffing or polishing; pickling and electrochemical polishing. A major defect of the mechanical polishing method is that the surface layer is contaminated with abrasive material (polishing paste) and particles which are formed during polishing and which destroy the oxide film. Before polishing, the sample surface has deep, narrow fissures and recesses, and also thin, sharp projections which become filled or covered with paste (or abrasive particles) and particles of the metal and the oxide film during polishing with paste or a wetting abrasive powder. Therefore, after polishing, the surface layer is not metallic, but rather, cermetic and glass-like, both in structure and luster.

During pickling and electrochemical polishing, the metal is contaminated with hydrogen, and its surface layer, with electrochemical corrosion products.

In processing the surfaces of samples these defects may be overcome if the samples are polished on solid (baked or preferably fused) abrasive discs or plates in the form of shaving hones. For many metals and alloys, mirror glass 1-2 cm thick with a special degree of polishing may be used, in which case, a powdery abrasive used by glass blowers for polishing and vacuum grinding edges should be used. Discs of boron carbide, titanium, and other metals, sintered from a batch of metals or oxides, are suitable for polished harder metals and alloys.

The polishing of samples with sintered or fused abrasive discs, preliminarily ground to the necessary roughness, is just as it is done with emery paper; but the sample must be shifted to a fresh place on the abrasive disc each time so that it will not be scratched due to the rubbing of metal against metal. When the whole surface of the disc is used, the layer of metal adhering to it is washed with a rag wet with alcohol, and the disc may be used again. With such a method of dry polishing, the discs themselves are actually not worn, the grain of the abrasive is not ground off, and consequently, the surface of the metal is not contaminated with

abrasive particles, etc. The degree of roughness attained by such
polishing is quite suitable for both kinetic and electronographic
studies. The initial roughness, as stated above, affects only the
kinetics of the first stage of oxidation at high temperatures, but,
beginning with some thickness of the oxide film which is character-
istic for each metal and for the conditions of oxidation, it is
determined by the course of the oxidation process itself. The
roughness created on the surface of a coating during the process
of oxidation in a wide temperature range (400-1,300°) is quite
satisfactory for electronographic and electron microscope studies.

Before polishing, the samples should be carefully degreased
by washing in pure acetone (twice distilled at low temperatures)
or benzene, after which they are transferred to glass containers
or cups for storage or for being fastened in special containers
with clean, degreased forceps. After polishing the surface of the
sample is observed under a standard biological microscope, and any
particles adhering to the surface are carefully removed with a
strip of ash-free filter paper. In determining the dimensions of
the sample with a micrometer, and also during weighing and other
subsequent operations, precaution must be taken against contamina-
tion of the surface by grease and dust. Before weighing, the sam-
ples should be washed by consecutive immersions in 3-4 jars filled
with pure acetone or benzene. It is still better to wash the sample
in a flow of these solvents. It is especially difficult to prepare
samples of thin tin sheets or tin foil for kinetic studies on micro-
balances, without contamination (by gases or greases). Degreasing
by pickling or electropolishing leads to contamination by gases and
oxides. In attempting to remove dissolved gases by heating in vacuo,
chemical compounds may form on the metal surface due to the presence
of both dissolved and residual gases. Therefore, the best samples
for studying the oxidation kinetics of metals with microbalances
(with a sensitivity of 10^{-7} to 10^{-8} g) are thin metal films con-
densed on a target suspended from the balance arm of the micro-
balance itself. If the foil or thin tin sheet is prepared by roll-
ing in vacuo on polished and carefully degreased rollers, then sam-
ples in the form of thin strips of this material can be more or
less easily degreased by electron bombardment or by a glowing elec-
tric discharge in an inert gas (spectrally pure argon). Both of
these methods of processing the surface of samples have been used
by D. V. Ignatov since 1945/46 in his studies of the oxidation
process in an electric gas discharge $\boxed{9}$, and since this time,
the method has been used by the authors as the most effective
method of removing all surface contaminations from samples. In
this process, the sample is suspended from one of the balance arms
of the balance because the degasification process is directly con-
trolled according to weight loss, and as soon as uniformity of sam-
ple weight is attained, degasification is stopped.

Chapter II

EXPERIMENTAL DATA

1. Oxidizability of Base Components and Binary Alloys

Nickel. By electronographic and x-ray studies of oxide sur-
face films of samples, many authors $\underline{/6}$, 17, 55, 56$\underline{/}$ have shown that
only one type of oxide, NiO, is formed during the oxidation of
nickel in air and oxygen. The possible occurrences of other nickel
oxides, Ni_3O_4 and Ni_2O_3, during the oxidation of metallic nickel
have not been evident. The nickel oxide NiO crystallizes into a
lattice of the cubic system of the rock salt type, with the $\underline{/}$lat-
tice$\underline{/}$ constant a = 4.1684 Å $\underline{/57}$.

Electronographic study of the structural transformations in
thin nickel films, prepared by vaporization and condensation on
cold substrates (mica or rock salt) in vacuo, shows the presence of
a nickel oxide on films in contact with oxygen at room temperature.
On electronograms, along with the diffraction rings characteristic
of nickel, rings characteristic of NiO have been discovered. The
intensity of the lines of the oxide increases with temperature,
but that of the metal decreases. After 30 minutes at 400° a
nickel film ∿ 500 Å thick is completely oxidized in air. In this
event, the structure of the oxide remaining corresponds to the
structure of NiO $\underline{/6}\underline{/}$.

According to our data, bulk samples of electrolytic nickel,
oxidized 30 minutes in air at temperatures ranging from room tem-
perature to 1,000°, and covered by nickel oxide NiO. On electrono-
grams of unheated samples and those heated to 100°, no oxide lines
were discovered; but rather, the whole electronogram was that of
nickel. On electronograms of samples heated to 200°, along with
the characteristic diffraction pattern of nickel, NiO lines were
discovered. Electronograms of the surface of samples oxidized at
300-1,000° for 30 minutes correspond to pure nickel oxide NiO.

After 11 hours oxidation at 600° an oxide film is formed on
the surface of electrolytic nickel, the former consisting of NiO
layers from the oxygen-air to the metal-oxide boundary. At 700-
800° after 11 hours of oxidation, i.e., at an oxide film thickness
of several microns, a thin oxide layer dissimilar to NiO was dis-
covered on the surface of the oxide film formed on electrolytic
nickel. The structure of this film is analogous that of spinel
(Figure 3a and b). Recrystallization of the surface oxide had
been noticed at 700°. At 800° its diffraction rings consists of
points, which attests to a high degree of recrystallization. The
oxide films, formed on electrolytic nickel at 700-800° and lying
under this thin surface layer, consist of NiO in all layers up to
the metal-oxides boundary (Figure 3b).

Magnetic properties, occurring at the same time at 800-
1,000° on the surface of the oxide coating, were discovered by
the deflection of an electron beam. At 900-1,000° the magnetic
properties of the surface oxide were so strong that a diffraction
pattern of the surface layer of the oxide film could not be ob-
tained. After removing the surface layer of the oxide film by
carefully scraping it with a razor blade, the magnetic properties
of the sample disappeared. The remaining part of the oxide film
under this layer, up to the metal-oxides boundary, consisted of
NiO.

Upon checking the validity of the prediction that the oxides
formed on the surface of the oxide film at 700-800° were nickel
oxides of the spinel type, and not impurities in the electrolytic
nickel, the experiments in the oxidation of nickel at 800° were
repeated with samples of high purity carbonyl nickel. The car-
bonyl nickel samples were prepared from the powdered metal. These
samples were heated at 800° in air for 11 hours, but no oxides of
the spinel type mentioned above were formed. The heating period
was prolonged, and every 5 hours an electronogram of the surface
was made. After 40 hours, the surface of the carbonyl nickel sam-
ples began to show magnetic properties; and on the surface of the
oxide film, oxides differing from NiO in structure appeared.

The new oxide phase on the nickel surface, having a struc-
ture unlike that of spinel and exhibiting high magnetic properties,
could not be determined either with electronographic or radiographic
methods. Due to the interaction of the magnetic field of the elec-
tron beam with the established magnetic field of the new oxide,
electronograms of sample surfaces coated with this thin oxide film
were either very hazy or not obtained at all. Roentgenograms were
also not obtained because this oxide film was too thin.

Upon oxidizing nickel in oxygen under a pressure of 1 mm Hg
at 300-700° for 1 hour /56/, only one oxide with the structure of
NiO was formed on its surface. In this case, the diffraction pat-
terns obtained at 300-400° were diffuse; whereas, those obtained
at 500-700° were sharp. At 600-700° some orientations in the oxide
film were observed, in which case, they discovered by the lapse of
~30 minutes after heating was begun, i.e., upon attaining some
definite thickness of the oxide film. In thin oxide films no ori-
entations were observed. Cooling the oxidized nickel samples in
hydrogen leads to partial reduction of NiO /16/.

V. I. Arkharov /17/ has established by x-ray analysis that,
in the film formed on nickel at 1,000°, the parameters of the lat-
tice of nickel oxide NiO in contact with the metal are less than
at the surface; and that the size of the grain at the surface of
an oxide coating is larger than that at the boundary with the metal.
On the basis of these results, Arkharov concluded that, in the
process of high temperature oxidation of nickel, oxygen diffusion

is predominant from the intermediate points of the NiO lattice to the metal. The front of the oxidation reaction, in his opinion, is the metal-coating /oxide/ boundary. Diminution of the grain size and the parameters of the crystal lattice of the oxide is caused by compression on all sides from the moment of its /the crystal lattice/ formation.

In other works on the oxidation mechanism of nickel, for example /3, 58/, on the basis of theoretical considerations the conclusion is made that the factor which determines the oxidation rate of nickel is the diffusion of Ni^{+2} ions along the vacant cation points of the oxide lattice.

To solve the problem of whether nickel ions diffuse to the outer surface of the coating or whether oxygen diffuses to the metal surface through the film in the nickel oxidation process, B. Ilschner and G. Pfeiffer carried out the following experiment /59/: A platinum wire 0.03 mm thick was fastened to a sheet of nickel and the sheet was heated at $1,000°$ in air for 48 hours; afterwards, the sheet was cut perpendicularly to the platinum wire. The cross section of the oxide film was studied under a microscope, and the wire was found to be in the middle of the oxide film, i.e., the film had grown both inward and outward, and had a thickness greater than the diameter of the wire. The oxide film consisted of two layers having different microstructures. The platinum wire was located at the boundary of the two layers. On this basis, the authors concluded that the two layers of the film were formed by two different mechanisms. According to the data of R. Lindner and A. Akerstrom /52/, the diffusion of Ni in NiO at $1,140-1,400°$ is described by the equation $D = 2.8 \cdot 10^6 e^{-119,500/RT}$ cm^2/sec, i.e., the diffusion rate at these temperatures is sufficiently high.

Many works on the study of the kinetics of nickel oxidation have been published /58, 60-62/. From these it follows that the rate of nickel oxidation changes within wide limits depending on the degree of purity of the metal. Kinetic data on the oxidation of nickel of varying purity have been generalized by O. Kubashev-skiy and O. Gol'dbek /60/. According to the data given by these authors, purer nickel (99.67% and 99.75%) is oxidized at a rate ten times less than that containing 1.2-1.5% of different impurities; but, according to the data of Ye. A. Gul'bransen and K. F. Andrew /58/, the rate constants of nickel oxidation at a given temperature may vary by 1,000 times. The activation energy of nickel oxidation, according to data of different authors /62/, varies approximately between 43,550 and 55,500 cal/mole. Up to $300°$ the time dependence of the growth of an oxide film on nickel is described by a logarithmic function /63/. A number of authors have found that at temperatures in the range of $600-1,000°$ the time function of nickel oxidation is parabolic /58, 60-62/.

According to the data of Gul'bransen and Andrew /58/, the function of nickel oxidation under a pressure of 7.6 cm Hg at

400-700° is parabolic, in which case the rate constant decreases
with the course of the oxidation process. The greatest changes
in the /rate/ constant during the course of time take place in
the temperature range of 400-550°. The authors offer two possi-
ble explanations for the time dependence of the rate constant:

1) The concentration of impurities inside the oxide de-
creases with oxidation time, as a result of which, the number of
vacant points for diffusion in the oxide lattice changes;

2) For the given stages of the reaction, the predominant
factor is diffusion along the grain boundary.

The oxide crystals grow in proportion to the thickening of
the oxide film, and at a certain thickness of the coating, the ef-
fect of diffusion along the grain boundary becomes small in com-
parison with diffusion through the oxide lattice.

Kinetic experiments carried out by the authors on the oxida-
tion of electrolytic nickel in air at 600-1,000° with 11 hours oxi-
dation at each temperature interval, showed that at 700-900° the
growth of the oxide film was a parabolic function /of time/. At
temperatures of 600 and 1,000°, the oxidation function deviated
from parabolic. At 600° the function tended to become logarithmic,
and at 1,000°, linear. The activation energy of the oxidation of
electrolytic nickel, computed from the graph of log k - 1/T, was
52,600 cal/mole.

As stated above, a small amount of impurities, and also,
the composition of the oxidizing medium, play a large role in the
kinetics of nickel oxidation. L. Horn /64/ studied the effect of
small additives on the oxidation rate of nickel; results of the
investigation are shown in Table 1.

TABLE 1

RELATIVE CRITICAL RATE CONSTANTS PER 1% ATOMIC WEIGHT OF ADDITIVE

Additive	Atomic Radius of Additive	Amount of Additive, % Atomic Weight	$\dfrac{(K_x - K_{Ni}) \cdot 10^6}{\text{% At. Wt. of Additive}}$
Be	1.13	1.22; 2.85; 5.25; 9.07; 13.1	17
Ca	1.97	0.07; 0.24; 0.26	216
Al	1.43	1.08; 2.87; 3.63; 6.96	15.8
Si	1.34	0.47; 1.26; 1.79; 4.25	102
Ti	1.45	0.24; 0.55; 1.05; 3.25	78.7

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Additive	Atomic Radius of Additive	Amount of Additive, % Atomic Weight	$\dfrac{(K_X - K_{Ni}) \cdot 10^6}{\%\ \text{At. Wt. of Additive}}$
Zr	1.60	0.076; 0.258; 0.289; 0.546	204
Ce	1.82	0.076; 0.15; 0.19; 0.72	275
Th	1.80	0.035; 0.063; 0.12; 0.24	383
Cr	1.28	2.18; 4.62; 6.57; 8.9; 9.1; 10.5; 21.2	48.2
Mo	1.40	0.3; 0.7; 2.0; 4.3; 6.1; 14.5	26.5
W	1.41	0.13; 0.29; 0.97; 2.26; 3.25	66.5
Mn	1.35	1.06; 1.87; 4.0; 7.25; 9.3	35.5
Cu	1.28	1.94; 4.77; 9.41; 27.6	24.4
Au	1.44	0.15; 0.296; 0.695; 1.54	7.3

Here, K_X is the rate constant for the oxidation of the alloys of nickel and the respective metal, and K_{Ni} is the rate constant for the oxidation of nickel.

Table 1 shows that all the additives increase the oxidation rate of nickel, in which case, the oxidation increases sharply with the addition of a few tenths of a percent of thorium, niobium, wolfram, titanium, tantalum, molybdenum, copper, or aluminum to nickel. Further increases in the amount of additive beyond the limits shown in Table 1 do not increase the oxidation rate. Chromium, silicon, beryllium, and cesium in small amounts increase the oxidation rate of nickel, by larger amounts lower it. Zirconium, gold, and manganese increase the oxidation rate in direct proportion to their concentration in the nickel.

On the basis of these experimental results, Horn concludes that the influence of small amounts of additive on the oxidation of nickel consists not only in the formation of metallic oxides of the additive in the film but also in the inclusion of odd types of atoms in the nickel lattice, in which case, the greater the difference between the atomic radii of Ni and the added metal the more marked is the increase in the rate of nickel oxidation.

Larger amounts of additives (10% or more) of manganese, molybdenum, or copper lower the heat resistance of nickel, but chromium, niobium, tantalum, or platinum additives increase it $\underline{/ \ 5 \ \underline{/}}$.

The presence of vapors of such metallic oxides as MoO_3 and Li_2O in the oxidizing atmosphere also affect the oxidation rate of nickel. Thus, the rate constant of nickel oxidation in oxygen under a pressure of 760 mm Hg at 1,000° in the presence of Li_2O is lowered fourfold /65/. The presence of MoO_3 vapors in the atmosphere increases the oxidation rate of nickel.

Chromium. The known chromium oxides Cr_2O_3 and CrO_3 are formed by the direct oxidation of chromium. CrO_3 is formed in a strongly oxidizing medium (ozone, or by electric discharge in a gas). Cr_2O_3 is formed by oxidation in air or pure oxygen; wherein, two modifications of this oxide are described /66, 67/: $\alpha = Cr_2O_3$, rhombohedral; and $\gamma = Cr_2O_3$, cubic. In coating, on chromium and its alloys, only the rhombohedral modification of chromium oxide is found, the parameters of its crystal lattice being $\alpha = 5.38$ and $\alpha = 55°17'$ /57/. Thermodynamically, chromium oxide $\alpha = Cr_2O_3$ is extremely stable and does not dissociate in a vacuum at $\sim 10^{-6}$ mm Hg at 1,000° /68/.

In comparison with other metals, chromium has good heat-resistance properties. According to the data of Gulbransen and Andrew /68, 69/, chromium is oxidized in oxygen at a pressure of 7.6 cm Hg and in the temperature range of 700-800° in accordance with a parabolic function. The activation energy for oxidation under these conditions for high purity electrolytic nickel is 66,300 cal/mole, and for chromium 99.8% pure, 37,500 cal/mole. The high oxidation rate of nickel observed at 900° decreases at high temperatures; but at 1,050°, the oxidation rate again increases sharply. The activation energy for oxidation of 99.8% pure chromium at 1,000-1,100° is 59,400 cal/mole. The graph of log k - 1/T shows a discontinuity in the curve between 900 and 1,000°.

Chromium is vaporized at a noticeable rate in vacuo at temperatures above 815°. At 950° the vaporization rate of chromium equals its oxidation rate. This temperature corresponds to the transition range on the graph of log k - 1/T. The presence of an oxide or an nitride film on the sample surface does not lower the vaporization rate in the temperature interval of 885-1,015°. At 800° and above, in vacuo, carbon contained in chromium reacts with the surface oxide to form CO; and the decarbonization of Cr occurs /68, 69/.

The authors studied the oxidation kinetics of electrolytic chromium in air at 600-1,000°. At 600-800°, after initial rapid oxidation, a stage of slow interaction between chromium and air develops. The increase-in-weight -- time curve does not conform to a parabolic function. At 900-1,000° the function of the growth of an oxide film on Cr is parabolic. The activation energy of oxidation at these temperatures, computed from the graph of log k - 1/T, is 70,500 cal/mole.

In comparing the oxidation kinetics of chromium in oxygen and air at the same partial pressure, it follows that the oxidation rate in oxygen is considerably higher than in air. According to Arkharov's data, chromium is oxidized at 700° in oxygen at a rate of 0.03 mg/cm^2 · hr, and in air, at 0.008 mg/cm^2 · hr.

V. I. Arkharov has studied the structure of the film formed on chromium during its high temperature oxidation in air and in oxygen $/17, 70/$. The coating on chromium, formed during oxidation in oxygen, consists entirely of $\alpha = Cr_2O_3$. On Debye $/$crystallo$/$-grams of weakly oxidized samples also, there were no lines which differed from chromium lines and $\alpha = Cr_2O_3$ lines. On radiograms of chromium weakly oxidized in air, which exhibited a well expressed textural type (111) parallel to the surface of the sample, besides chromium and $\alpha = Cr_2O_3$ lines, a supplementary reflection of great intensity in the form of a diatropic blackening maximum of d = 1.37 Å was received. On radiograms of chromium samples strongly oxidized in air, this maximum persisted in all cases when radiograms were made of those inner layers of the coating which adjoined the metal surface.

First, this maximum was recorded as a cubic oxide of Cr $\gamma = Cr_2O_3$. Thus, Arkharov considered that, between the metal layer and the outside layer of the coating, there was an oxide interlayer consisting of $\gamma = Cr_2O_3$. From this, Arkharov predicted that the front of the chromium oxidation reaction was at the oxides-metal boundary. The primary oxidation product is the intermediate oxide phase of $\gamma = Cr_2O_3$. It is formed by the orientational reorganization of the metal lattice upon its inclusion of atoms which diffuse through the oxide film. In proportion to its further oxidation, $\gamma = Cr_2O_3$ is transformed into the stable form $\alpha = Cr_2O_3$.

In more recent work, the compound found at the metal-coating boundary of samples oxidized in air was interpreted as a nitride of chromium, Cr_2N. Besides this, it was discovered that there was an increase in the parameter of the crystal lattice of Cr_2O_3 formed on chromium in air in comparison to that of Cr_2O_3 formed in oxygen. From this, the earlier proposed mechanism of chromium oxidation was reconsidered and it was accepted that the diffusion of chromium through the oxide phase did not take place to a marked degree. The oxidation of chromium in air is accomplished by the diffusion of nitrogen and oxygen atoms through the oxide film to the metal, in which case the front of the reaction of nitrogen with chromium Cr/Cr_2N precedes that of oxygen with chromium. The slower oxidation of chromium in air than in oxygen is explained by the difficulty of oxygen diffusion through Cr_2O_3 containing dissolved nitrogen. The oxidation reaction takes place at the Cr_2N/Cr_2O_3 boundary $/70/$.

Electronographic studies carried out by the authors on the structure of oxide films formed on bulk samples of electrolytic

chromium in air, and also, on the structure of thin films formed on chromium by vaporization and condensation in vacuo, showed the following:

Electronograms of unheated thin films of chromium in contact with air at room temperature showed, besides the diffraction pattern of chromium, one very weak diffuse ring not related to chromium. On electronograms obtained from chromium films after heating the latter 30 minutes at 100°, two "extra" diffuse rings, unrelated to the reflection from chromium, were discovered. The intensity of these "extra" rings was very weak. The interarea distances corresponding to these rings were ~ 2.56 and 1.24 Å. At higher heating temperatures up to 300° the intensity of the "extra" rings on the electronograms increased. However, the 'extra" rings remained diffuse. On the electronogram of films heated at 300°, there were three "extra" rings, of which, the first and second rings were hard to differentiate because the difference in their diameters was 1.8 mm, and the width of the lines was ~ 0.9 mm. On the microphotogram of the corresponding part of this electronogram, there were two maxima (and not one) of 23.4 and 25.2 mm in the distance from the center. The corresponding interarea distances were 2.671 and 2.480 Å, which almost correspond to the interarea distances of the known strong reflections from chromium oxide $\alpha = Cr_2O_3$ (2.67 and 2.47 Å), to which, these rings should be attributed also. Besides the two reflections stated, there was one diffuse other diffuse extra ring ($d \approx 1.23$ mm) of very weak intensity, which complicated its interpretation. The remaining rings on this electronogram corresponded to reflections from chromium.

After 30 minutes at 400° a ~ 500 Å thick chromium film is oxidized completely. The structure of the oxide formed corresponds to chromium oxide $\alpha = Cr_2O_3$. With further increases in heating temperature up to $1,000^\circ$ the structure of the oxide remains the same, i.e., $\alpha = Cr_2O_3$.

No chromium oxide lines were discovered on the electronograms of unheated bulk samples, the diffraction pattern being entirely that of the metal. Oxide lines also did not appear on the electronograms of chromium samples heated at 100 and 200° for 30 minutes. These patterns had a strong background. The diffraction pattern of bulk samples of chromium heated 30 minutes at 300° belonged entirely to chromium oxide $\alpha = Cr_2O_3$. With temperature increase up to $1,000^\circ$, the structure of the oxide on the chromium samples did not change, but the diffraction pattern became sharper, and the lines became thicker and resolved into points, which indicated growth of the oxide grain.

The structure of oxide films on bulk chromium samples heated 11 hours at $600-1,000^\circ$, in all layers of the oxide film, from the oxides-air boundary to the oxides-metal boundary, corresponded to the oxide $\alpha = Cr_2O_3$. The nature of the diffraction patterns of

both the surface and the inner layers of the coating indicated the recrystallization of the oxide films under these conditions.

Ye. A. Gulbransen and J. Hicman /56/ also discovered only one oxide, α = Cr$_2$O$_3$, on the surface of electrolytic chromium oxidized in oxygen 1-60 minutes at a pressure of 1 mm Hg at 300-700°. At 300-400° the pattern was diffuse, and at 500°, medium sharp. At 400-700° orientations were observed. Upon cooling the oxidized samples in hydrogen, no types of chemical or physical transformations were noticed.

According to the data of Lindner and Akerstrom /52/, the diffusion rate of chromium in chromium oxide Cr$_2$O$_3$ at 1,000-1,350° is rather high. The diffusion equation is as follows:

$$D = 4 \cdot 10^3 e^{-160,060/RT} \text{ cm}^2/\text{sec}.$$

Apparently, small amounts of impurities affect the oxidation rate of chromium. This follows from the work on Gulbransen and Andrew /68, 69/, and also from comparing data on the oxidation rates of chromium. According to the data of Arkharov and others ·/70/, chromium in oxygen at a pressure of 160 mm Hg is oxidized at a rate ten times that in the experiments of Gulbransen and Andrew /68, 69/ where the pressure was 76 mm Hg. It is possible that, here, the pressure of the oxygen played a role.

The effect of small amounts of impurities on the oxidizability of chromium has not been studied in detail. Large amounts of additives (over 10%) of tantalum, nickel or niobium increase the heat-resistance of chromium, but molybdenum, tungsten, and titanium lower it /5/.

Nickel-Chromium. Nickel-chromium alloys containing approximately up to 8-9% atomic weight of chromium are oxidized at a higher rate than pure nickel, in which case, the oxidation rate of these alloys increases with chromium concentration up to 6% atomic weight. Table 2 gives data on the oxidation rates of nickel-chromium alloys at 1,000° /7/.

TABLE 2

THE OXIDATION RATE OF NICKEL-CHROMIUM ALLOYS AT 1,000°
WITH HEATING TIME 57,600 SECONDS

Cr, % Wt.	Increase in Weight $(\frac{\Delta m}{A}) \cdot g/cm^2$	$K = \frac{1}{t} (\frac{\Delta m}{A})^2$
--	$4.1 \cdot 10^{-3}$	$3.1 \cdot 10^{-10}$
0.3	$8.8 \cdot 10^{-3}$	$14.0 \cdot 10^{-10}$

Cr, % Wt.	Increase in Weight $(\frac{\Delta m}{A}) \cdot g/cm^2$	$K = \frac{1}{t} (\frac{\Delta m}{A})^2$
1.0	$12.3 \cdot 10^{-3}$	$26.0 \cdot 10^{-10}$
3.0	$13.4 \cdot 10^{-3}$	$31.0 \cdot 10^{-10}$
10.0	$2.9 \cdot 10^{-3}$	$1.5 \cdot 10^{-10}$

According to the data of Horn $/64/$, the "oxidation rate constant - % wt. of chromium" curve has a sharp maximum at a composition of $\sim 6\%$ of chromium. The constant for an alloy with 10% Cr nearly equals the oxidation rate constant of nickel.

Results of studies of the service life of nickel-chromium alloys at 1,050° with Cr content of 2-20% $/13/$ also substantiate a minimum heat-resistance at $\sim 6\%$ Cr. Over 5% of chromium lengthens the service life. Figure 5 shows the dependence of the service life on the composition of the alloy. The service life index is defined by Hessenbruch $/18/$ as the number of heatings up to 1,050° or switch-offs of the current running through an 0.4-mm-diameter wire, before burning it out.

Figures 6 give data on the heat-resistance of alloys containing 10-80% Cr in the temperature range of 700-1,102° $/72/$. These data are plotted in terms of curves of increase-in-weight in $g/m^2 \cdot hr$; and a Ni-Cr structural diagram is given as well. From this figure it follows that, in a Υ-solid solution, the oxidation rate of alloys decreases with increases in Cr content and is minimal for a composition with a normal Cr content in the Υ-solid solution. Upon transition into the heterogeneous range $\Upsilon + \beta$, the oxidation rate increases with chromium content.

Other authors have reached the same conclusions $/73/$. However, alloys of 80% Ni + 20% Cr are widely used in practice. This is due to the fact that technical alloys usually contain small amounts of impurities and special additives of various elements, which shift the boundary of Cr solubility in the solid solution to the side of lower chromium content. Therefore, addition of over 20-25% of Cr does not improve heat-resistance. Moreover, the technical properties of an alloy with over 25% Cr content are considerably worse than at lower Cr content.

The twofold effect of Cr on the heat-resistance of Ni-Cr alloys is explained by K. Hauffe as due to the fact that, at up to $\sim 6\%$ at. wt. of Cr, one phase-expressed oxide, NiO, occurs during oxidation. Chromium oxide, dissolved in the nickel oxide, according to the theory of Wagner, leads to an increase in the concentration of vacant Ni^{+2} points in the coating, as a result of which, the diffusion rate of metallic ions in the coating increases. Therefore, the oxidation rate of the alloy increases also.

At higher Cr content in the alloy (over 6% at. wt.), the oxidation rate is lowered with increases in Cr concentration. This lowering of the oxidation rate is conditioned by the arising of a phase in the oxide film with a spinel-type structure -- $NiCr_2O_4$, in which exchange-of-place processes between the ions take place unusually slowly. Hauffe considers that the resistance of Ni-Cr to oxidation is directly connected with the formation of the chemical compound of the oxides $NiCr_2O_4$, and not with the formation of a pure Cr_2O_3 phase, because the latter quickly vaporizes at high temperatures (above 1,000°) $\overline{/3}$, 4, 74$\overline{/}$.

Literary data on the heat-resistance of binary Ni-Cr alloys, and on the composition and structure oxide of films on their surfaces, is rather contradictory.

C. Smitels, S. Williams, and J. Avary $\overline{/73/}$ have compared the compositions of oxide films on Ni-Cr alloys containing 10-40% Cr with their heat-resistances. Using x-ray analysis, these authors discovered that the composition of the oxide film generally did not correspond to that of the alloy. In coatings on binary Ni-Cr alloys, the content of Cr_2O_3 quickly increased with the concentration of Cr in the alloy. Internal oxidation along the grain boundary of the alloys was strongly expressed in alloys with low Cr content. After 10 hours oxidation at 1,000° in air, mixtures of the oxides NiO, Cr_2O_3, and $NiCr_2O_4$ were found on the surface of the alloys in different proportions, depending on the composition of the alloy, in which case, the $NiCr_2O_4$ content in the oxide films was negligibly small. The Cr_2O_3 and NiO contents in the oxide films in given in Table 3.

TABLE 3

COMPOSITIONS OF OXIDE FILMS ON NICKEL-CHROMIUM ALLOYS
AFTER 10 HOURS OXIDATION AT 1,000° $\overline{/73/}$

% Cr in Alloy	% Cr_2O_3 in Coating	% NiO in Coating
10	10	90
20	80	20
30	90	10
40	90	10

In studying the dependence between the composition of oxide films and service life, the authors concluded that those alloys were most heat-resistant which had surface oxide films containing

not less than 50% Cr_2O_3. Higher chromium oxide content did not improve oxidation resistance. I. Itaka and S. Mijake [75], in studying the structure of the oxide film occurring on an 80% Ni-20% Cr alloy at high temperature, discovered an oxide with the structure of spinel $NiCr_2O_4$. In their opinion, good heat-resistant properties of a Ni-Cr alloy are conditioned by the formation of $NiCr_2O_4$ during the oxidation process of the alloy. Chalmers and Quarrell [76] also found that the oxides formed on Ni-Cr alloys at temperatures above 1,000° also have spinel-type structure.

H. Holler [77] showed that the electrical resistance of heaters of an 80% Ni-20% Cr alloy, measured while the heater was cold, was lowered after service life tests which consisted in alternately heating and cooling between 950 and 200°; and that this lowering of resistance was conditioned by a considerable decrease in the Cr content of the alloy. Thus, the Cr content in the heater material, prepared from an alloy with 18.4% Cr, was lowered to 8.5%. Qualitative analysis of the oxide film on the heater revealed only chromium oxide -- no nickel was found in the film. Holler considers that, in his experiments, the atmosphere (the air in the tubular furnace) was substantially oxidizing and selective oxidation had not necessarily occurred, and that the loss of chromium from the alloy was due to its higher vaporizability and more rapid diffusion to the surface of the sample (as compared to nickel).

Hicman and Gulbransen [1] have used the electronographic method to determine the structures of oxide films on 80% Ni + 20% Cr alloys in dependence upon time and temperature with heating in 1 mm Hg of oxygen. Maximum heating time was 1 hour. From the results obtained by these authors, it follows that a Ni-Cr alloy at over 300° never has a nickel oxide film, NiO. At 400-700° the structure of the oxide film corresponds to chromium oxide Cr_2O_3. The electronograms obtained at 300° were very diffuse and the lines were very small; therefore, the authors could not determine the structure of the oxide film formed at this temperature interval. In a more recent work, Hicman reports that, on the surface of an 80% Ni + 20% Cr alloy oxidized in 1 mm Hg of oxygen at 300-400°, nickel oxide NiO is formed, and at 500-800°, chromium oxide Cr_2O_3 [2]. J. Moreau and J. Bernard [78] studied the structures of coatings on alloys containing 5.7 and 10% Cr, oxidized in air at 800-1,300°. After prolonged oxidation, two-layer outer coatings were formed on the alloys. The outer layer of the coating at the air boundary consisted of NiO; the inner layer, extending to the surface of the alloy, consisted of a $NiO-NiCr_2O_4$ mixture, in which case, the oxide $NiCr_2O_4$ seemed to be interspersed in the general NiO mass as a different type of grain. A layer in the form of Cr_2O_3 particles interspersed in almost pure nickel was found under the outer coating.

The authors have made kinetic and electronographic [electron diffraction] studies of the oxidation mechanism of 80% Ni + 20% Cr

alloys in air. Oxidation kinetics were studied at temperatures of 600-1,000°. The samples were heated for 25 minutes and 25 hours; in the latter case, the samples were periodically cooled after every 4-5 hours.

Results of the kinetic studies on oxidation are shown in the "weight increase - time" curves in Figure 7. The oxidation curves at 600 and 700° are logarithmic. After first increasing in weight rapidly, the weight increase of the samples approached a limiting value.

The "weight increase - time" curve has no horizontal section at 800°. At this temperature a limiting increase-in-weight value was not found.

At 900 and 1,000° the curves are parabolic, and some scattering of points is observed. The rate constants of the parabolic time function of oxidation have the following values: at 900° the constant equals $5.9 \cdot 10^{-12}$ $g^2/cm^4 \cdot sec$; and at 1,000°, increases to $2.4 \cdot 10^{-11}$ $g^2/cm^4 \cdot sec$.

Figure 8 shows a graph of the temperature dependence of the weight increase. For comparison, the "weight increase - temperature" curve for Cr after an equal oxidation time is shown on this same graph. It is apparent from the curves in Figure 8 that 80% Ni + 20% Cr alloy samples undergo less weight increase at 800,900 and 1,000° than Cr samples, and that the difference in the weight increases of Cr and the alloy samples increases with temperature.

On the surface of 80% Ni + 20% Cr alloys oxidized 30 minutes in air, coatings of the following compositions are found: at 300 and 400°, mainly nickel oxide NiO; at 500, 600 and 700°, chromium oxide $\propto = Cr_2O_3$; and at 1,000°, an oxide of the spinel type, $NiCr_2O_4$.

Results of the electronographic analysis of oxide films formed on the surface of 80% Ni + 20% Cr alloys oxidized 25 hours are shown in Table 4 which indicates that, at 600 and 700°, all layers of the oxide film, from the oxide-air boundary to the oxide-alloy boundary, consist of chromium oxide $\propto = Cr_2O_3$. At 800° a two-layer oxide film forms on the sample surface. The outer layer of this film (at the oxide-air boundary) consists of a double oxide with a spinel-type structure which corresponds to $NiCr_2O_4$. The inner layer of the oxide films, extending to the alloy surface, consists of chromium oxide $\propto = Cr_2O_3$. The thickness of the $NiCr_2O_4$ oxide layer is small in comparison to that of the $\propto = Cr_2O_3$ layer. A two-layer oxide film forms on the sample surface at 900 and 1,000° also. Its outer layer consists of $NiCr_2O_4$, and the inner layer, of $\propto = Cr_2O_3$. The $NiCr_2O_4$ layer at 900° comprises almost one-half of the over-all thickness of the film, and at 1,000°, almost the entire thickness. A thin chromium oxide $\propto = Cr_2O_3$ layer is only found in contact with an alloy.

In accordance with the foregoing statement, a structural diagram of oxide films on the surface of 80% Ni + 20% Cr alloy

TABLE 4

COMPOSITIONS OF OXIDE FILMS FORMED ON THE SURFACE
OF AN 80% Ni + 20% Cr ALLOY AFTER 25 HOURS OXIDATION
IN DEPENDENCE UPON TEMPERATURE

Temperature, °C	600	700	800	900	1,000
On the outer surface of the oxide film	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$NiCr_2O_4$	$NiCr_2O_4$	$NiCr_2O_4$
In the middle of the oxide film	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$NiCr_2O_4$	$NiCr_2O_3$ [sic!]
On the boundary with the alloy	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$ (thin film)

samples is shown in Figure 9. Alloys of 80% Ni + 20% Cr were sub-
ject to internal oxidation. Figure 10 shows a metallographic photo
of the microsection of an 80% Ni + 20% Cr alloy sample with the
oxide film formed on its surface after 25 hours at 1,000°. The
photo shows that, under the outer coating of the oxide, there is
an undercoating consisting of oxide particles located mainly along
the grain boundary of the alloy.

From this it follows that, in a case of the oxidation of
Ni-Cr alloys under conditions of excess oxygen, oxides of both Ni
and Cr are formed on the alloy surfaces. During oxidation of these
same alloys in weakly oxidizing media, or under conditions of a
limited oxygen supply, the selective oxidation of Cr occurs. This
phenomenon was studied on alloys of compositions 80% Ni + 20% Cr
and 90% Ni + 10% Cr by N. Spooner, J. Thomas, and L. Thomassen
/72/. When wires of the stated alloy compositions were oxidized
at 800-1,000° in a gas mixture (16% H$_2$; 10% CO; 4% CO$_2$; 1% CH$_4$;
1.5-2.5% H$_2$O; the remainder, N$_2$) or in air, being placed inside
narrow thermocouple tubes, selective oxidation of chromium was ob-
served, in which case, the oxide formed along the grain boundary,
resulting in the rapid destruction of the alloys. When oxidized
alloy samples of 90% Ni + 10% Cr were heated at 800-1,000° in tubes
of small diameter, the oxide coating on the samples was transformed
into a light metallic outer layer or into an alloy layer rich in
nickel, under which, a green oxide was discovered along the grain
boundary of the alloy.

The authors of this study attribute this phenomenon to the
establishment of a thermodynamic equilibrium expressed by the equa-
tion $NiO + Cr$ (in the alloy) $\rightarrow Ni + Cr_2O_3$.

To verify this fact, the following experiment was carried out: An oxidized nickel foil and an unoxidized 90% Ni + 10% Cr alloy sample were heated at 980° in an evacuated quartz tube. After a few hours the nickel oxide on the foil was completely reduced to metallic nickel. The alloy sample gave a typical diffraction pattern of the selective oxidation of Cr along the grain boundary, in which case the alloy had taken on magnetic properties as a result of the loss of much Cr (the Curie point for a Ni-Cr alloy at room temperature corresponds to 7% Cr). By weighing the samples before and after the experiment, it was established that the loss in weight from the nickel foil approximately equalled the weight increase of the alloy sample.

J. Moreau and J. Bernard /80/ studied the selective oxidation of a Ni-Cr alloy with 4.6% Cr at 800-1,250° in a $H_2O + H_2$ mixture at ratios $P_{H_2O}/P_{H_2} = 6.5 \cdot 10^{-3} - 5.9 \cdot 10^{-2}$.

Under these conditions only the chromium is always oxidized. The surfaces of oxidized samples were studied by the microscopic and electronographic methods. At the lower partial pressures of H_2O and at 900°, the alloy sample was uniformly covered along each grain with chromium oxide particles with an average size of 1 micron. Under these conditions, the degree of oxidation depends on the orientation of the crystals. At high temperature and partial pressure of H_2O, an increase in the dimensions of the oxide particles and a decrease in their number is first observed, and then, the particles begin to grow together in parallel lines. Along with this, different outgrowths, for example, ridges /or perhaps "whiskers"/ less than 1 micron tall, whose form depended upon the orientation of the crystals, appeared on the sample surface between the particles. Finally, at 1,200° and at $P_{H_2O}/P_{H_2} = 4.20 \cdot 10^{-2}$ the formation of bits of a compact oxide, randomly distributed over the sample surface, was observed. Their distribution and structure was not connected with the crystal structure of the metal. In the experiments, carried out at constant temperatures, all the described oxidation stages were passed through in the course of time, in which case, ridges appeared on the metal surface at those points where fine oxide grain had been earlier, but these disappeared due to their coagulation into a coarse metal grain. The authors surmised that the disappearance of the oxide from certain places on the surface of the sample was cuased by vaporization. Part of the oxide then precipitated in some places on the sample, which facilitated the growth of some parts of the crystal oxide; the other part of the vaporized oxide precipitated onto the walls of the furnace. Upon further oxidation, a Cr_2O_3 oxide layer whose thickness increased with time grew on the sample surface.

2. The Influence of Some Components
on the Oxidizability of Alloys

Carbon. The role of carbon consists, on one hand, in combining with Cr in chromium carbide, and subsequently, in the impoverishment of the Υ-solid solution by Cr $/\overline{1}8/$; on the other hand, carbon reduces metallic oxides by the formation of CO at high temperature. Gaseous carbon monoxide evolving from the oxide film of the alloy, destroys it. In a high vacuum, decarbonization reactions of Ni-Cr alloys begin at 840° $/\overline{8}2/$. Carbon lowers the heat resistance of alloys, and its negative influence increases with its concentration in the alloy. Thus, 0.3% C by weight in a Ni-Cr alloy at 1,050° almost reduces its service life twofold $/\overline{1}8, 8/$.

Silicon and Manganese. A detailed investigation of the effect of silicon and manganese and also their joint effect on Ni-Cr alloys has been made by Gulbransen, et al. $/\overline{8}4$-$86/$.

Electronographic $/$electron diffraction$/$ analysis of oxide films on these alloys showed that the compositions of the coatings were the same with both alternate heating and cooling and with oxidation at constant temperature. Table 6 shows the results of the structural analysis of the coatings. These data were obtained by electron diffraction by reflection from the surfaces of oxidized samples and by passage $/$of the electron beam$/$ through oxide films separated from the samples.

It should be emphasized that no oxides of silicon were found in the coatings on the alloys. It is possible that the silicon oxide SiO_2 exists in the coating at the boundary with the alloy $/$i.e., at the alloy-coating boundary$/$ in the form of an amorphous layer which does not lend itself to structural analysis.

As shown in Table 5, under conditions of alternate heating to 1,175° and cooling, alloys containing 1.3% Si have a service life twice as long as those with 0.30% Si. The service life of alloys containing 1.70% Mn and 0.30% Si is 3.5 times less than that of alloys without Mn but with the same content of Si. The presence of 1% of Si in the alloys completely surpresses the negative influence of Mn. In cyclic tests at 1,177°, the service life of alloys containing 1.03% Si and 0.05% Mn in one, and 1.01% Si and 2.3% Mn in the other, were the same.

During oxidation at constant temperatures of 500-900° in 7.6 mm Hg of oxygen, the least weight increase was shown by alloy 12246 (0.30% Si; 0.01% Mn). The weight increase of alloy 12046 (1.39% Si; 0.01% Mn) at 850° was almost twice as much, and at 900°, 1.5 times as much as that of alloy 12246. Alloy 13246 (1.7% Mn; 0.30% Si) showed the highest weight increase.

From this it follows that Si has a very important effect on the structure of the oxide film and a very strong effect on the service life. The effect of Mn on the structure of oxide films is

F
5
9

TABLE 5

COMPOSITIONS AND SERVICE LIFE OF Ni-Cr ALLOYS [84-86] AT TEST TEMPERATURE 1,175°

Alloy	C	Mn	Si	Cr	Ni	Fe	Zr	Ca	Mg	Al	Service Life, hrs
					Percentage Composition						
12046	.08	.01	1.39	19.9	bal.	.34	.10	.024	--	.07	157
12246	.08	.01	.30	19.98	"	.32	.05	.029	--	.08	86
13246	.12	1.7	.30	19.98	"	.20	--	--	.006	--	25

TABLE 6

COMPOSITIONS OF COATINGS FORMED ON Ni-Cr ALLOYS
DURING OXIDATION IN OXYGEN FOR 1-60 MINUTES [82]

Alloy	Temperature, °C						
	400	500	600	700	800	900	950
12046	NiO	NiO (1 min) + Cr_2O_3 (5-60 min)	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3 + spinel ? ($NiCr_2O_4$)	Cr_2O_3
12246	NiO	NiO	Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3 + spinel ($NiCr_2O_4$?)	Cr_2O_3 (1-5 min) Cr_2O_3 + spinel ($NiCrO_4$?) (30-60 min)
13246	NiO	NiO	Cr_2O_3 + $MnCr_2O_4$	Cr_2O_3 + $MnCr_2O_4$	$MnCr_2O_4$	MnO + $MnCr_2O_4$ (1 min) $MnCr_2O_4$ (5-60 min)	900° Cr_2O_3 (1-5 min) $MnCr_2O_4$ + Cr_2O_3 (30-60 min)

rather significant. If Si and Ca are absent in the alloy, then Mn substantially shortens the service life. The authors of these studies concluded that, during cyclic tests with alternate heating and cooling of the samples, the compositions of the coatings did not play a decisive role, but rather, the physical compositions of the alloy-coating boundaries.

As B. Lustman has shown /87/, intensive internal oxidation takes place during the oxidation of alloy 1204-6. Internal oxidation is considerably less in alloy 12246; and in alloy 13246, internal oxidation was not discovered. Figure 11 shows lateral microsections of oxidized samples of these alloys. Lustman considers that the role of Si during tests under conditions of alternate heating and cooling consists in the formation of subcoatings, as a result of which, good adhesion of the coating to the alloys is effected /87/. The lowered heat-resistance of Ni-Cr alloys by the addition of large amounts of Si (over 2-2.5%) is explained by the formation of a large number of silicon oxides in the coating, which lowers its melting point /18/.

In this way, Si has a twofold effect on the heat-resistance of Ni-Cr alloys. In small amounts (less than 2%), it lengthens the service life of alloys at 800-1,175° /18, 83-87/; and in amounts over 2-2.5%, Si sharply lowers the heat-resistance of Ni-Cr alloys /83/, the strongest effect of Si on the heat-resistance of alloys occurring with alternate heating and cooling. At constant temperature the effect of Si is less marked /86/.

Mn lowers the heat-resistance of Ni-Cr alloy. A strong effect is shown by even tenths of a percent of Mn; whereas, with further increases in Mn content, its effect diminishes /18/.

Molybdenum and Tungsten (73). Coatings on alloys of 10% Cr + 5-20% W + Ni (remainder) contain tungsten oxide. Tungsten oxide was not found in the coatings on alloys containing 20% Cr + 5-20% W + Ni (remainder).

Tungsten in the amount of 5% shortens the service life of an 80% Ni + 20% Cr alloy at 1,100°. With further increases in W content of over 5% the service life lengthens, and for an alloy with 10% W, it is approximately twice as long as that of a binary 80% Ni + 20% Cr alloy.

For a Ni-Cr alloy with 10% Cr, the service life is also lowered at a 5% W concentration; however, further increase in W concentration does not effect improved heat-resistance.

The effect of Mo is analogous to that of W. The lowering of heat-resistance by Mo is more marked than that by W /73/.

Alkaline Earth Elements. Beryllium in the amount of 0.2-1.2% has little effect on the service life of 80% Ni + 20% Cr alloys at 1,050° /18/. It also does not have a marked influence on the oxidation rate of 80% Ni-20% Cr alloys in air at 900°. Intense internal oxidation was discovered in Ni-Cr-Be alloys /18/.

Magnesium and Lithium increase the heat-resistance of Ni-Cr alloys /18/.

Calcium considerably increases the service life of Ni-Cr alloys. The addition of 0.5% Ca (to the furnace charge) increases the service life fourfold at 1,050° /18/. Nichrome with Ca added is unusually resistant to action of lead oxide Pb_2O, and the deformed (hot rolled) alloy is still more resistant than the cast alloy /81/. The effect of adding Ca to a nickel alloy consists in the improved adhesion of the coating to the alloy /88/. Calcium oxides were not found on the coatings.

Rare Earth Elements. Among those additives which improve the heat-resistance of Ni-Cr alloys, a mixture of rare earth elements, in alloy compositions of about 45% Cr, 30% La, 20% Nd + Pr, and 5% Yb, is distinguished by its own singular influence. Cerium alone also has considerable effect. Thus, the addition of 0.2% Ce increases the service life of a Ni-Cr alloy 9-10 times /18/.

The influence of the addition of cerium consists mainly in improving the adhesion of the coating to the alloy /88/.

Zirconium lengthens the service life of a Ni-Cr alloy to about the same degree as magnesium. Thorium greatly increases the heat-resistance of a Ni-Cr alloy. Thorium is in third place after cerium and calcium in increasing service life. Tantalum also has a positive influence, but it is somewhat less than that of zirconium and magnesium /18/.

Vanadium lowers the heat-resistance of alloys. The results of W. Hessenbruch /18/ on the service life of Ni-Cr alloys in dependence upon their content of small amounts of different additives are shown in Figure 12.

Aluminum. The authors have studied the kinetics of the thermal oxidation of Ni-Cr alloys with Al additive at 600-1,000° with heating time of 25 hours at each temperature (Table 7). The results obtained are shown in Figures 13-14 in the form of "oxidation rate - temperature" and "oxidation rate - Al-concentration-in-the-alloy" curves.

The differences in the nature of the oxidation of alloys containing 1% Al and those without Al are small. The shapes of "weight increase - time" curves are the same at all temperatures, but the oxidation rate at the same heating temperatures is less for an alloy containing Al than for a binary alloy.

The oxidation kinetics of the same alloy containing 4.18% Al is in sharp contrast to that of a binary alloy. The logarithmic shape of the "weight increase - time" curves for an alloy containing 4.18% Al is maintained up to 900°. The oxidation rates of alloys containing 7.22 and 10% Al are very low up to 1,000°. Up to 1,000° inclusive, there are near horizontal sections on the "weight increase - time" curves of these two alloys, i.e., after the rapid weight increase of the sample during the first hours of oxidation, its further weight increase drops sharply.

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TABLE 7

THE CHEMICAL COMPOSITION (%) AND MICROSTRUCTURE*
OF Ni-Cr-Al ALLOYS

Alloy No.	Cr	Al Synthesis	Al Analysis	Ni	Microstructure
1	20	0	--	Remainder	Υ = solid solution
2	20	1	--	"	"
3	20	5	4.18	"	Υ + Ni$_3$Al (start of the separation of the second phase)
5	20	7.5	7.22	"	Υ + Ni$_3$Al
6	20	10.0	--	"	Υ + Ni$_3$Al

* The microstructure of alloys is given per the data of I. I. Korni-
lov and L. I. Pryakhina.

Figures 13 and 14 show the average oxidation rates of alloys
after 25 hours. It is apparent from Figure 13 that the temperature
dependence of the oxidation rate of alloys with different Al con-
tents is the same. The "oxidation rate - temperature" curve for
Alloy Nr 2 (1%) differs little from an analogous curve for Alloy
Nr 1 (without Al). The shape of "oxidation rate - temperature"
curves for alloys containing 4.18; 7.22 and 10% Al is essentially
different from that of alloys containing 1% and no Al, beginning
at 800°. For alloys containing 4.18; 7.22 and 10% Al, the oxida-
tion rate in dependence upon temperature increases more slowly in
the temperature range of 800-900° than in the ranges of 700-800
and 900-1,000°. In the temperature range of 900-1,000°, the slopes
of "oxidation rate - temperature" curves for alloys containing large
amounts of Al is considerably less than the slopes of analogous
curves for alloys without Al.

From the curves showing the dependence of the oxidation rate
of alloys on their Al content, it follows that Al lowers the oxida-
tion rate at all temperatures. The oxidation rates of alloys con-
taining 4.18 and 10% Al are about the same up to 900°. At 1,000°
the oxidation rate of alloys containing 1-7.22% Al drops almost
linearly with increases in their Al content. Further increase in
the Al content of the alloy did not have an essential influence of
the oxidation rate.

TABLE 8

COMPOSITIONS OF OXIDE FILMS ON Ni-Cr-Al ALLOYS OXIDIZED 30 MINUTES

Temp., °C	4.18% Al	10.0% Al
400	NiO	NiO
500	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$
600	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$
700	$\alpha = Cr_2O_3 + NiCr_2O_4$	Spinel, $\alpha = 8.30$ Å
800	Spinel, $\alpha = 8.30$ Å	Spinel, $\alpha = 8.27$ Å
900	Spinel, $\alpha = 8.27$ Å	Spinel, $\alpha = 8.24$ Å
1,000	Spinel, $\alpha = 8.21$ Å	Spinel, $\alpha = 8.21$ Å

The compositions of oxide films formed on Ni-Cr-Al alloys
with 4.18 and 10% Al during 30 minutes oxidation are shown in
Table 8, and the compositions of coatings on Ni-Cr-Al alloys,
formed during 25 hours oxidation, are shown in Table 9.

From the data in Table 9, it follows that oxide films on
alloys with 1% Al content do not differ in structure, within the
limits of accuracy, from oxide films formed on a binary alloy of
80% Ni + 20% Cr (see Table 5). On the surface of alloys samples
with 4.18 and 7.22% Al at temperatures of 700-1,000°, coatings
are formed which consist of oxides of spinel structure, in which
case, the constants of spinel change from 8.30 to 7.9 Å in depen-
dence on temperature and the place that the given layer is located
in the oxide film. The closer the oxide film layer is to the al-
loy-coating boundary, the lesser is the lattice constant of the
spinel which constitutes this layer. And the higher the tempera-
ture of heating the samples and the higher their Al content, the
lesser are the lattice constants of the spinels which constitute
the oxide films.

Taking into account the possible formation of spinels
$NiCr_2O_4$ ($\alpha = 8.31$ Å), $NiAl_2O_4$ ($\alpha = 8.05$ Å) and $\gamma = Al_2O_3$ ($\alpha =
7.89$ Å), one may consider that oxides of the spinel type, arising
on these alloys with the lattice constant changing from 8.30 to
7.9 Å, are solid solutions of these three spinels. The lessening
of the lattice constant of the solid solution of the spinels, ap-
parently, may be explained by the increase of aluminum oxide con-
centration in the solution. From this it also follows that the

TABLE 9

COMPOSITIONS OF OXIDE FILMS FORMED ON THE SURFACE
OF Ni-Cr-Al ALLOYS DURING 25 HOURS OXIDATION

% Al in Alloy	Layer	600	700	Temperature, °C 800	900	1,000
1	I	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$NiCr_2O_4$	Spinel	Spinel, $\alpha = 8.27$ Å
	II	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	Spinel	Spinel, $\alpha = 8.27$ Å
	III	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	$\alpha = Cr_2O_3$	Thin layer of $\alpha = Cr_2O_3$
4.18	I	$\alpha = Cr_2O_3$	Spinel	Spinel, $\alpha = 8.30$ Å	Spinel, $\alpha = 8.27$ Å	Spinel, $\alpha = 8.21$ Å
	II	$\alpha = Cr_2O_3$	--	--	Spinel, $\alpha = 8.20$ Å	Spinel, $\alpha = 8.14$ Å
	III	--	--	Spinel	Spinel, $\alpha = 7.9$ Å	Spinel, $\alpha = 7.9$ Å
7.22	I	$\alpha = Cr_2O_3$	Spinel	Spinel, $\alpha = 8.25$ Å	Spinel, $\alpha = 8.22$ Å	Spinel, $\alpha = 8.19$ Å
	II	--	--	--	--	Spinel, $\alpha = 8.03$ Å
	III	--	--	Spinel, $\alpha = 7.9$ Å	Spinel, $\alpha = 7.9$ Å	Spinel, $\alpha = 7.9$ Å
10	I	--	--	--	--	Spinel, $\alpha = 7.9$ Å
	II	--	--	--	--	--
	III	--	--	--	--	Spinel, $\alpha = 7.9$ Å

nearer the oxide film layer to the alloy-coating boundary, the higher its aluminum oxide concentration; and the higher the Al content in the alloys and the higher the heating temperature, the higher also is the aluminum oxide concentration in the film formed on the surface of the sample. The general characteristics of diffraction patterns of spinel-type oxides with different values of the parameters of the crystal lattice are unequal. Figures 15-18 show electronograms /electron diffraction patterns/ of spinel-type oxides with constants α = 8.30 and 7.9 A, and for comparison, diffraction patterns of thin $NiCr_2O_4$ and γ = Al_2O_3 films.

Metallographic photographs of lateral microsections of Ni-Cr-Al alloy samples oxidized 25 hours at 1,000° are shown in Figures 19-21, which show that alloys containing 1% Al undergo almost the same degree of internal oxidation as a binary 80% Ni + 20% Cr alloy (see Figure 10). A sublayer in the form of oxide particles interspersed in the alloy is formed under the outer layer of the oxide film. From an analogous photograph (Figure 20) of an alloy sample containing 4.18% Al, it is apparent that internal oxidation takes place in the sample also; however, the process is considerably weaker than in the first case. Figure 21 shows an alloy containing 7.22% Al, in which case, internal oxidation did not occur and the oxide film being formed is uniform in thickness.

Thus, the effect of Al on the rate of isothermal oxidation of Ni-Cr alloys in air takes place at temperatures over 700°. In this same temperature range /over 700°/ differences were found in the oxide films on an 80% Ni-20% Cr and Ni-Cr-Al alloys. Besides, the presence of more than 4% Al prevents internal oxidation between the crystalline grain of Ni-Cr alloys. It follows from these data that the role of Al consists in increasing the protective properties of an oxide film on Ni-Cr-Al alloys.

According to the data of Hessenbruch /18/ Al also lengthens the service life of a nichrome alloy at 1,050° (see Figure 12). Besides this, Al retards the reaction rate of sulfur with Ni-Cr alloys.

Niobium. The authors' study of the oxidation kinetics of alloys in air with a fixed content of 20% Cr, 6% Al and varying niobium content (2.5; 5 and 10%) showed that niobium retards the oxidation rate of these alloys up to temperatures of 800° inclusive. Beginning at 900°, the "weight increase - time" curves for Ni-Cr-Al-Nb alloys containing 5 and 10% Nb, shown in Figures 22 and 23, have irregular shapes. The oxide film on the alloy seems to lose its protective properties from time to time. The weight increases of alloys containing Nb are greater than those of alloys without Nb.

The structures of oxide films, arising on Ni-Cr-Al-Nb alloys during 1 hour oxidation in air and determined by electronography of the surface coatings, are given in Table 10.

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TABLE 10

OXIDE FILMS ON Ni-Cr-Al-Nb ALLOYS

Tempera-ture, °C	% Content of Niobium in Alloy		
	2.5	5.0	10
400	NiO	NiO	NiO
500	NiO	NiO	NiO
600	α = Cr$_2$O$_3$	α = Cr$_2$O$_3$	α = Cr$_2$O$_3$
700	Spinel, α = 8.30 Å	Spinel, α = 8.30 Å	Spinel, α = 8.30 Å
800	Spinel, α = 8.27 Å	Spinel, α = 8.27 Å	Spinel, α = 8.27 Å
900	Spinel, α = 8.26 Å	Spinel, α = 8.26 Å	Spinel, α = 8.26 Å
1,000	Spinel, α = 8.20 Å	Spinel, α = 8.20 Å	Unestab-lished

The table shows that the compositions of the surface coat-
ings of the three Ni-Cr-Al-Nb alloys are the same. Niobium oxides
in the form of an individual phase were not found in the coating.
It is altogether possible that niobium oxides were present in the
inner layers of the oxide film or existed in the film as solid solu-
tions or as chemical compounds with other oxides.

From this material it follows that these alloys are less
heat-resistant than Ni-Cr-Al alloys. The marked lowering of the
heat-resistance of Ni-Cr-Al-Nb alloys at 1,000° is probably con-
nected with the fact that, at this temperature, the rates of forma-
tion of free niobium ions and their diffusion through the oxide
film take on essential value. In the coating a considerable amount
of niobium oxide is formed. Oxides of Nb exhibit a high volume
ratio (ratio of the oxide volume to the volume of metal used), and
therefore, the presence of niobium oxide in a film creates such
high pressures that the film begins to crumble. Thus, with the
presence of niobium oxide in the surface of an oxide film, the
latter will have no protective properties.

According to the data of G. V. Akimov and A. A. Koselev
[81], Nb lowers the oxidation rate of Ni-Cr alloys in air at 900°.

Titanium. The compositions of Ni-Cr-Ti alloys, the oxida-
tion of which was studied in air by the authors using gravimetric
and electronographic methods, are given in Table 11.

TABLE 11

CHEMICAL COMPOSITION (%) AND MICROSTRUCTURE*
OF Ni-Cr-Ti ALLOYS

Alloy No.	Cr	Ti	Ni	Microstructure
1	20	0.68	Remainder	γ - solid solution
2	20	3.44	"	γ + Ni_3Ti (onset of the deposition of the second phase along the grain boundary of the alloy)
3	20	5.88	"	γ + Ni_3Ti
4	20	9.76	"	γ + Ni_3Ti

* Microstructure is given per data of I. I. Kornilov and L. J. Pryakhin.

The results of the investigation are shown in Figure 24 as "mean oxidation rate after 25 hours - temperature" curves. For comparison, an analogous curve for a binary 60% Ni + 20% Cr alloy is shown in the figure.

At 800, 900 and 1,000° the shapes of the "weight increase - time" curves indicate a continuous increase in sample weight after the onset of oxidation. However, the shapes of the curves are not parabolic. It should be noted that the oxidation rate of an alloy containing 5.88% Ti is less than that of one containing 3.44% Ti.

Figure 24 shows that a rapid increase in the oxidation rate of Ni-Cr-Ti alloys, depending upon temperature, begins at 700°, i.e., 100° lower than the corresponding temperature for an 80% Ni + 20% Cr alloy. This same oxidation rate for pure Ti drops sharply, beginning at 700°.

Electron diffraction study of the oxide films formed on alloys containing 3.44, 5.88, and 9.76% Ti and oxidized 1.2 and 3 hours at 400-900° showed that the coatings formed on the alloy samples were of the following compositions: at 400°, mainly NiO; at 500° on an alloy containing 9.76% Ti, titanium dioxide, TiO_2; and at 600, 700, 800, and 900° on all samples, TiO_2, with rutile structure.

Figure 25 shows a metallographic photo of the lateral micro-section of a Ni-Cr-5.88% Ti alloy sample oxidized 25 hours in air at 1,000°. The photo shows that intensive oxidation has taken place between the crystalline grain. In this case, the general pattern of the distribution of oxides in the subcoating differs

from that of oxides in the subcoating on an 80% Ni + 20% Cr alloy (see Figure 10).

According to the data of Hessenburg /18/, given in Figure 12, the addition of up to 1% of Ti slightly lowers the service life of Ni-Cr alloys at 1,050°.

Boron. The authors carried out kinetic and electron diffraction studies of the oxidation process of Ni-Cr alloys containing 0.007-0.50% B.

The kinetic study was carried out at 900 and 1,030°; heating time was 100 hours.

Marked differences in the oxidation kinetics of Ni-Cr alloys at 900° were not found. The shapes of "weight increase - time" curves were irregular, weight increases being accompanied by weight losses. Obvious differences in the oxidation kinetics of alloys containing little (up to 0.05%) and much (over 0.1%) B were observed at 1,030°. At this temperature also, the "weight increase - time" curves have irregular shapes, which indicates that weight increase due to oxidation is accompanied by weight loss. This irregularity in the shapes of the curves is considerably greater at 1,030° than at 900°. Especially high initial weight increases and subsequent weight losses were found in alloys containing 0.2-0.5% B. Rapid and high weight losses were observed after heating the samples 25-30 hours, when the coatings began to crumble from the samples.

Electronographic /electron diffraction/ study of the structures of oxide films on Ni-Cr alloys containing boron was carried out both after short oxidation time at 400-1,000° and after 100 hours oxidation at 900 and 1,030°. Differences in the structures of oxide films on alloys with different B content were not found.

Results of electron microscope study of secondary structures of oxide films are shown in Figures 26-29. Figure 26 is a photograph of the surface of the oxide film formed on an alloy sample containing 0.50% B after heating 100 hours at 900°. As the photo shows, the oxide film here is not a smooth and continuous coating. The surface shows many irregularly oriented polyhedra of the oxide. The size of the separate oxide crystals reaches 1 micron. The surface of the oxide film is broken up by deep fissures. The width of the fissures reaches 0.1 micron. The fissures are located both along the grain boundary and along the grain itself. The oxide film is perforated with tiny pores whose dimensions reach 100-200 Å.

Figure 27 shows a photograph of the surface of an oxide film formed on an alloy sample containing 0.007% B at 900° for 100 hours. Here there are also fissures and pores, however the number and size of the pores is less than in an alloy containing 0.50% B.

Figures 28 and 29 show photographs of the surfaces of samples heated over 100 hours at 1,030°. As stated above, the coating partially crumbles from the sample surface at this temperature. Thus,

the photographs give the image of the surface layer of the coating left on the sample. From these photos it follows that the defects of oxide films formed at 1,030° are more serious than those occurring at 900°. This applies especially to pores in the coating. Their dimensions reach 500-1,000 Å. In this connection, a larger number of pores and fissures was found in those samples which contained more B than in those containing less.

Interaction of Oxides. X-ray analysis of phases formed in the system Cr_2O_3-NiO, carried out on samples prepared from mixtures of Cr_2O_3 and NiO powders combined in different proportions and heated 1-2 hours at 1,000°, showed that only one chemical compound of the composition $NiCr_2O_4$ with spinel-type structure existed in the Cr_2O_3-NiO system /89/. Even with a slight excess of some oxide (nickel or chromium oxide) in the sample, a second phase, NiO or Cr_2O_3 respectively, was shown on the radiograms along with $NiCr_2O_4$, which lead the authors of the work /89/ to conclude that, at 1,000°, the solubility of nickel oxide and chromium oxide in $NiCr_2O_4$ was low and that chromium oxide was insoluble in nickel oxide.

K. Hauffe and K. Pschera /74/ attempted to establish the formation mechanism of spinels $NiCr_2O_4$, $NiAl_2O_4$ and others. For this purpose, samples of pure oxides, for example, NiO, Cr_2O_3, $NiAl_2O_4$, pressed from powders, were placed in the order shown in Figure 30, for example, for the system NiO-Cr_2O_3, and heated at 1,100° in air over 200 and 400 hour periods. The samples were weighed before and after heating. Marked change in the weight of samples was found in the system NiO-Cr_2O_3. Nickel oxide samples underwent weight increases, in which case, the weight increase of sample No 1 was 0.1-0.6 mg; of sample No 2, next to the spinel sample, 1.2-1.6 mg.

The $NiCr_2O_4$ sample (No 3), next to the NiO sample, underwent weight loss of 1.3-2.3 mg. The $NiCr_2O_4$ sample (No 4) almost did not change in weight.

The Cr_2O_3 samples lost weight, in which case, the one next to $NiCr_2O_4$ (No 5) lost almost 2.4 mg.

In tests where a 0.25 mm platinum disc was placed between the NiO and $NiCr_2O_4$ samples to prevent their direct contact, the change in weight of the samples was the same as in tests where they were in direct contact.

The authors give a simpler explanation of such a result by comparing the vaporizability of NiO with that of chromium oxide. Due to the relatively high vapor pressure of Cr_2O_3, not only in pure form but also in spinel form, the re-forming spinel grows, not on the surface of the initial spinel sample, but, on the surface of the nickel oxide NiO. The formation of new spinel on NiO samples was also discovered microscopically.

Thus, chromium oxide vaporized from $NiCr_2O_4$ settles on NiO samples. The formation of spinel on the surface of nickel oxide samples occurs by way of the counter diffusion of Cr^{3+} and Ni^{2+} ions.

In analogous tests with NiO, $NiAl_2O_4$ and Al_2O_3 oxides, the changes in weight were small; however, some evidence of the formation of new spinel on the surface of the aluminum oxide sample was obtained.

Hauffe and Pschera also studied the vaporizability of oxides in air at $1,100^\circ$.

As shown from the results of these experiments, the vaporization rate of aluminum oxide under these conditions is very low. The vaporization rate of each of the succeeding oxides is greater than that of the preceding: Al_2O_3, NiO, $NiCr_2O_4$, Cr_2O_3, and ZnO (Figure 31).

Electronographic /electron diffraction/ studies of phase transformations in the systems $NiO-Cr_2O_3$ and $NiO-Al_2O_3$ were carried out by D. V. Ignatov. In this work, the samples were thin two-layer oxide films obtained by the following method: First, Cr or Al films 300 Å thick were obtained by vaporization and condensation /of the metals/ in vacuo and oxidized in air up to complete transformation into $\alpha = Cr_2O_3$ and $\gamma = Al_2O_3$. Then, nickel which was also completely oxidized in air was condensed on each of these films in vacuo. The thickness of the initial layers of the metals was so chosen that the oxides formed from them would correspond to the stoichiometric composition of the compounds $NiCr_2O_4$ and $NiAl_2O_4$. In this way, the samples $\alpha = Cr_2O_3-NiO$ and $\gamma = Al_2O_3-NiO$. The samples for the system Cr_2O_3-NiO were further heated in air in the temperature interval $400-900^\circ$; and those for the system $\gamma = Al_2O_3-NiO$ were heated in the interval of $600-1,300^\circ$.

The change in phase composition of the samples in dependence upon temperature is shown in Table 12.

From these data it follows that, in the system $NiO-Cr_2O_3$, beginning at 700°, the formation of a chemical compound takes place. Its formation process under the stated conditions ends at 800°; and at 900°, the sample is destroyed apparently by recrystallization.

Upon heating bulk $NiCr_2O_4$ samples at $1,100$ and $1,200^\circ$ in air, the vaporization of chromium oxide $\alpha = Cr_2O_3$ from the spinel was observed. Upon heating bulk $NiCr_2O_4$ samples up to $1,100^\circ$ in vacuo at 10^{-6} mm Hg, the spinel decomposes into metallic Ni, nickel oxide NiO, and chromium oxide $\alpha = Cr_2O_3$.

The formation of spinel in the system NiO - $\gamma = Al_2O_3$ was found to begin at 800°. After 15 hours at 900°, the oxides films with general thickness of $800-900^\circ$ Å /see Note/ were almost completely transformed into spinel. The $NiAl_2O_4$ phase seemed stable up to $1,300^\circ$. /Note: The "degree" symbol after $800-900$ should be disregarded./

At $1,300^\circ$ the spinel $NiAl_2O_4$ decomposed into $\alpha = Al_2O_3$ and NiO, and at $1,300^\circ$, NiO vaporized from the sample. Electronograms /electron diffraction patterns/ of samples heated at $1,300^\circ$ indicated strong recrystallization of the oxide $\alpha = Al_2O_3$. In vacuo,

spinel $NiAl_2O_4$ decomposes into metallic nickel, nickel oxide, and aluminum oxide $\alpha = Al_2O_3$.

TABLE 12

CHANGE OF PHASE COMPOSITION IN THE SYSTEMS $NiO-Cr_2O_3$ AND $NiO-Al_2O_3$ IN DEPENDENCE UPON TEMPERATURE DURING 15 HOURS HEATING

Temperature, ^oC	$NiO-Cr_2O_3$	$NiO-Al_2O_3$
400	Mixture of $\alpha = Cr_2O_3$ and NiO	Mixture of $\gamma = Al_2O_3$ and NiO
500	"	"
600	Mainly the same mixture and a trace of $NiCr_2O_4$	"
700	$\alpha = Cr_2O_3$ and NiO and a noticeable amount of $NiCr_2O_4$	"
800	Mainly $NiCr_2O_4$ and traces of oxides NiO and Cr_2O_3	$\gamma = Al_2O_3$ and NiO and a noticeable amount of $NiAl_2O_4$
900	Destruction of sample	Mainly $NiAl_2O_4$ and traces of oxides NiO and Al_2O_3
1,000	--	$NiAl_2O_3$
1,200	--	$NiAl_2O_3$
1,300	--	$\alpha = Al_2O_3$

In considering the heats of formation of the oxides Cr_2O_3 and Al_2O_3, the author concluded that spinel $NiCr_2O_4$ if formed from the initial oxides by way of the counter diffusion of Ni^{2+} and Cr^{3+} ions. Spinel $NiAl_2O_4$ is formed mainly due to the diffusion of Ni^{2+} ions.

Recently, a number of works by Soviet and non-Soviet authors have appeared on the determination of the parameters of the diffusion of metals in oxides.

Of those works by non-Soviet authors, first of all, let us mention that of Lindner and Akerstrom /52/ on the investigation of the self-diffusion process of cations in oxide systems, using radio-isotopes. These authors studied the following oxide systems:

$NiCr_2O_4$, $ZnCr_2O_4$, $NiAl_2O_4$, $AnAl_2O_4$, NiO, and Cr_2O_3. The oxide samples were prepared from powders.

In a review article by Hedwall $/91/$, the results are given of the investigation of the diffusion of calcium in CaO, $\alpha = CaSiO_3$, $\alpha = Ca_2SiO_4$, and Fe_2O_4; zinc in ZnO and $ZnFe_2O_4$; lead in $\alpha = PbO$; iron in $ZnFe_2O_4$; and barium in $BaTiO_3$.

Of those works by Soviet authors, we should mention that of Borisenko and Ye. I. Morozov $/53/$ on the diffusion of Co in cobalt ferrites in the temperature interval of $950-1,350^\circ$. These authors showed that, at $1,125^\circ$, mainly boundary diffusion is exhibited. It was also established that the activation energy of diffusion is strongly dependent upon the composition of the oxide.

Also, the work of L. A. Shvartsman, P. L. Gruzin and O. A. Pechenev $/92/$ on the investigation of Fe^{59} diffusion in refractory materials at $1,120-1,330^\circ$ should be mentioned.

D. V. Ignatov, I. N. Belokurova and I. N. Belyanin $/54/$ studied the processes of Cr^{51} and Fe^{59} diffusion in spinels $NiCr_2O_4$ and $NiAl O$, and also the diffusion of these same elements in the oxides $\alpha = Cr_2O_3$ and $\gamma = Al_2O_3$. The investigations were carried out with samples pressed from powders and sintered, just as in all the works cited above.

The investigations of Ignatov and Votinova $/94/$ on the diffusion of iron in corundum (single crystal $\gamma = Al_2O_3$) and in ruby, i.e., in corundum with $\sim 0.5\%$ of Cr added, were carried out with fused samples of synthetic materials.

Variations in the results are explained both by differences in the samples used by different authors, and also, by the various conditions under which the experiments were carried out (Table 13).

TABLE 13

PARAMETERS OF DIFFUSION IN OXIDE SYSTEMS

Compound	Isotope	Q, cal/mole	D_0	Literary Source
NiO	Ni^{65}	119.5	$2.8 \cdot 10^6$	$/52/$
$NiCr_2O_4$	Ni^{65}	74.6	0.85	52
$NiCr_2O_4$	Cr^{51}	72.5	0.74	52
$NiCr_2O_4$	Cr^{51}	44.8	$2.03 \cdot 10^5$	54
$NiCr_2O_4$	Fe^{59}	61.0	$1.35 \cdot 10^{-3}$	54
$NiAl_2O_4$	Ni^{65}	55.0	$3 \cdot 10^{-4}$	52

Compound	Isotope	Q, cal/mole	D_Q	Literary Source
$NiAl_2O_4$	Cr^{51}	50	$1.17 \cdot 10^{-3}$	54
$\alpha = Cr_2O_3$	Fe^{59}	44.0	$4.95 \cdot 10^{-6}$	54
$\alpha = Cr_2O_3$	Cr^{51}	22.3	$4.29 \cdot 10^{-3}$	54
$\alpha = Cr_2O_3$	Cr^{51}	100.0	$4 \cdot 10^{3}$	52
$\alpha = Al_2O_3$	Fe^{59}	82.0	1.33	54
$\alpha = Al_2O_3$	Fe^{59}	91.4	1.826	94
Ruby	Fe^{59}	90.8	1.006	94
ZnO	Zn^{65}	74.0	1.3	91
$ZnCr_2O_4$	Zn^{65}	85.5	60	52
$ZnCr_2O_4$	Cr^{51}	81.0	8.9	52
$ZnAl_2O_4$	Zn^{65}	78.0	$2.5 \cdot 10^{2}$	52
$ZnFe_2O_4$	Zn^{65}	86.0	$88 \cdot 10^{2}$	91
$ZnFe_2O_4$	Fe^{59}	82.0	$8.5 \cdot 10^{2}$	91
FeO	Fe^{55}	29.7	0.118	93
Fe_3O_4	Fe^{55}	55.0	5.2	93
Fe_2O_3	Fe^{55}	112.0	$4 \cdot 10^{5}$	52
CaO	Ca^{45}	81.0	0.4	91
$CaFe_2O_4$	Ca^{45}	86.0	30	91
$CoFe_2O_4$	Co^{60}	65		53
$\alpha = CaSiO_3$	Ca^{45}	112.0	$7 \cdot 10^{4}$	91
$\alpha = CaSiO_4$	Ca^{45}	55.0	$2 \cdot 10^{-2}$	91
PbO	Pb	66.0	10^{5}	91
$BaTiO_3$	Ba^{140}	89.0	8.0	91

F
5
9

Compound	Isotope	Q, cal/mole	D_0	Literary Source
Magnesite	Fe^{59}	78.7	22.4	92
Chromomagnesite	Fe^{59}	28.4	$3.1 \cdot 10^{-5}$	92
Dinas	Fe^{59}	44.8	0.1	92

F
5
9

Chapter III

PRINCIPAL THEORIES OF THE OXIDATION OF METALS AND ALLOYS

A number of theories have been propounded to explain the oxidation process of metals and alloys. Some of these deal with the formation of thin oxide films, while others treat of the formation of thick films at high temperatures. The latter will be considered in this book. It is obvious that the mechanism of oxidation at low temperature and in the first stages of high temperature oxidation differs from that of the later stages of high temperature oxidation where an earlier formed oxide film of definite thickness is present. In the latter case, the oxidation of metals coated by a continuous oxide film, i.e., without fissures or pores, is accomplished by the diffusion of the metal (or oxygen) through the film. In a given range of temperature and oxygen pressure, and when conditions are such that the oxidation rate is determined solely by the rate of diffusion in the oxide, film growth as a function of time is parabolic. An explanation for the parabolic time function of film growth at constant temperature was given by Wagner $/96/$ and later developed by other authors (T. Hoar $/100/$, W. Jost $/101/$, and K. Hauffe $/3$, $4/$). Wagner's theory, based on the premises that metal ions diffuse along the crystal lattice of an oxide and that electrons are transferred in equivalent amounts by ions, proceeds from Frenkel's mechanism of the electroconductivity of oxide semiconductors. In accordance with this theory, oxides fall into two main groups according to their mechanism of electroconductivity: oxide semiconductors having a deficiency of metal, and those having an excess. In the lattice of an oxide of the first group, NiO for example, part of the cation points (Ni^{2+}) are left unoccupied, in which case the number of free points on the oxide-gas $/$oxygen or air$/$ boundary is greater than that on the metal-oxide boundary. Electrical neutrality is effected by the formation of metal ions of higher valence (Ni^{3+}). When there is a gradient in the concentration of unoccupied lattice points, the directed $/$selective$/$ diffusion of metal ions occurs in the film between the metal-oxide and oxide-gas boundaries. Metal ions move along the unoccupied cation points (along cation holes) of the lattice to the outer surface of the oxide film; and electrons also move to this surface -- along electron holes -- by means of electron exchange between cations of normal valence (Ni^{2+}) and those of higher valence (Ni^{3+}). Oxygen adsorbed at the oxide-gas boundary is ionized and combines with metal ions.

New oxide layers are formed in this manner. Wagner's equation for determining the rate of film (coating) growth in a general form (both for oxidation and for reactions of a metal with halogens or sulfur) appears as follows:

$$\frac{dn}{dt} = \left\{ \frac{300}{96,500} \cdot \frac{1}{Ne} \int_{\mu_0^i}^{\mu_0^a} \frac{1}{Z_2} (n_1 + n_2) \, n_3 x \cdot d\mu_\theta \right\} \frac{1}{\Delta\xi} = k''/\Delta\xi, \qquad (2)$$

where dn/dt is the number of metal ions diffusing outward toward
the oxide-gas boundary, or the number of anions diffusing toward
the metal-coating boundary over 1 cm^2/sec; $\Delta\xi$ is the thickness of
the film in centimeters; N is Avogadro's number; e is the charge
on the element in absolute electrostatic units; Z_2 is the valence
of the anion; μ_0 is the chemical potential of oxygen; μ_0^i, the chemi-
cal potential of oxygen at the metal-oxide phase boundary; μ_0^a, /the
chemical potential of oxygen/ at the oxide-oxygen boundary; x is
the electroconductivity in units of 1/ohm $\cdot$ cm; and n_1, n_2, and n_3
are the transfer numbers of cations, anions and electrons. In this
case, according to Wagner, it is understood that only metal ions
diffuse during oxidation. Oxygen ions cannot diffuse because their
dimensions considerably exceed those of metal ions. The expression
in the braces in equation (2) is called the "rational constant of
oxidation rate" and is equal to the rate of oxide formation in gram-
equivalents per sec over 1 cm^2 at an oxide film thickness of 1 cm.
It follows from equation (2) that the diffusion rate, and subse-
quently, the oxidation rate depends upon the transfer numbers of
the ions, which is in turn connected with the concentration of va-
cant points, i.e., holes, in the oxide lattice. The more vacant
points in the lattice, the greater the diffusional flow of metal
ions and the higher the oxidation rate. If the number of lattice
vacancies decreases, due, for example, to a change in oxygen pres-
sure or to the introduction of alien ions into the oxide lattice
with valences differing from those of the ions of the metal under-
going oxidation, then the oxidation rate decreases. On this basic,
Wagner extended the theory of the oxidation of pure metals to in-
clude the oxidation of binary alloys, which was carried out more
completely by Hauffe /3, 4/. In studying the effect of an alloy-
ing element on the oxidation rate of an alloy base component, the
mechanism of the conductivity of its oxide should be considered.
In cases of the formation of oxides with cation holes in the lat-
tice (NiO, Cu_2O, FeO, CoO and others), the oxidation rate is propor-
tional to the mobility and concentration of cation holes. If, in
the first approximation, it is considered that the diffusion of
metal ions does not depend on the content of alien ions in the
oxide lattice, then the oxidation rate is a linear function of the
concentration of cation vacancy points: oxidation rate increases
and decreases with their (vacancy point) concentration. Only a
single-phase oxide film containing NiO is formed on an alloy during
oxidation in the concentration range or up to ~6% at. wt. of Cr.
Ni^{+2} ions at NiO crystal lattice points are partially replaced by

Cr^{3+} ions, which increases vacancy point concentration. This follows from the results of the Wagner-Zimens study $\underline{/71/}$. Using Hauffe's symbols $\underline{/3}$, $4\underline{/}$, $x^{o}_{Ni\square}$ " indicates the Ni^{2+} vacancy point concentration in pure nickel; $x_{Ni\square}$ ", that in a solution of Cr_2O_3 in NiO; $x_{\bullet}$, the concentration of Ni^{3+} ions; $x_{Cr\bullet(Ni)}$, the concentration of Cr^{3+} ions replacing Ni^{3+} ions in NiO lattice points; x_{Cr}, Cr concentration in the alloy; and it is considered that $x_{Cr\bullet(Ni)} = x_{Cr}$. Upon observing the conditions for electrical neutrality in the oxide films of the stated alloys, the number of Ni^{2+} vacancy points is determined by the formula

$$x_{Ni\square} " = \frac{1}{2} x_{\bullet} + \frac{1}{2} x_{Cr\bullet(Ni)}.$$

Accepting the approximation that

$$x_{Ni\square} " \approx \frac{1}{2} x_{Cr},$$

because

$$x_{Cr} = x_{Cr\bullet(Ni)} \gg x^{o}_{Ni\square} ",$$

we derive a relationship between the oxidation rate constant k of the alloy and that of pure nickel, k^{o}:

$$k/k^{o} = x_{Cr}/2x^{o}_{Ni\square} ".$$

At a Cr concentration of 6% at. wt. in an alloy, the oxidation rate decreases with increases in Cr concentration. This decrease in oxidation rate is conditioned by the development of a film phase with spinel structure of the $NiCr_2O_4$ type, in which, the process of ion exchange proceeds unusually slowly. Hauffe considers that the resistance of Ni-Cr alloys to oxidation is due to the formation of a chemical compound of the oxide $NiCr_2O_4$, and not due to the formation of a pure Cr_2O_3 phase, because the latter quickly vaporizes at high temperatures (over 1,000°) $\underline{/74/}$.

Alloys of Ni with monovalent lithium, in a Li concentration range where a single-phase NiO film is formed on the alloy during the oxidation process, would be oxidized at a slower rate than pure Ni because the presence of Li ions in nickel oxide NiO reduces the number of vacancy points in the lattice of the latter. The relationship of the oxidation rate constants of an alloy and of pure nickel equals the expression

$$\frac{k}{k^{o}} \approx (\frac{x^{o}_{Ni\square} "}{x_{Li}})^2 ,$$

if $x_{Li\bullet(Ni)} = x_{Li} \gg x^o_{Ni\square}$ ",

where x_{Li} is the Li concentration in the alloy; and $x_{Li\bullet(Ni)}$ is the concentration of Ni^{2+} points occupied by Li^+ ions.

The influence of alloying elements on the oxidation rate of metals is opposite to that of oxides of the NiO type when oxides with an excess of metal with respect to stoichiometric composition (ZnO for example) are formed during oxidation. In these oxides, the excess cations and an equivalent number of electrons are located in the interstices of the crystal lattice points. Adding small amounts of metals to zinc, the valence of the former exceeding that of zinc, Al for example, leads to a decrease in the number of Zn^{2+} ions in the lattice interstices as a result of the displacement of Zn^{2+} ions by Al^{3+} ions at the points of the ZnO crystal lattice. And since the factor which determines the oxidation rate of zinc is the rate of diffusion of zinc ions along the lattice interstices, the latter rate being proportional to the number of Zn^{2+} ions in the interstices, the addition of Al leads to a lowering of the oxidation rate of Zn. Alloys of Zn containing 0.1-1% at. wt. of Al are oxidized at a rate 100 times slower than pure Zn. The relationship of the oxidation rate constants of Zn-Al alloys and pure zinc, assuming that

$$x_{Al\bullet(Zn)} = x_{Al} \gg x^o_{Zn\dot{O}} \, ,$$

is expressed by the formula

$$k/k^o \approx x^o_{Zn\dot{O}}/x_{Al} \, ,$$

where $x_{Al\bullet(Zn)}$ is the concentration of Al^{3+} ions replacing Zn^{2+} ions in ZnO lattice points; x_{Al} is the Al concentration in the alloy; and $x^o_{Zn\dot{O}}$ is the concentration of Zn ions in the interstices of the pure oxide ZnO.

If a monovalent metal, Li for example, is added to zinc, then the replacement of Zn^{2+} ions by Li^+ ions in ZnO crystal lattice points leads to an increase in the number of Zn^{2+} ions in the interstices of ZnO lattice points. Therefore alloys of zinc with lithium are oxidized at a higher rate than pure zinc. Zinc alloys containing 0.4% at. wt. of Li are oxidized at a rate 100 times faster than pure zinc, under analogous conditions. The relationship of the oxidation rate constants of Zn-Li alloys and of zinc is determined by the expression

$$k/k^o \approx x_{Li}/x^o_{Zn\dot{O}} \, .$$

In some cases, when an oxide with an insufficient number of anions forms on a metal, i.e., its lattice contains vacant anion points (TiO_2), Hauffe states that the oxidation rate of this metal

is determined by the rate of anion diffusion. The influence of an alloying element is analogous that in the case of the formation of an oxide film of the ZnO type.

The influence of vapors of oxides and metallic salts in the atmosphere on the oxidation rate is analogous to the influence of these metals when they are introduced into the alloy as additives.

Thus, from this theory it follows that the nature of defects in the oxide lattice, resulting from the oxidation of a given alloy or metal, should be taken into account when introducing into an alloy additives intended to improve (i.e., increase) the heat-resistance of the alloy.

One possible explanation for the logarithmic function of film growth on metals have been given by U. Evans $/96/$. Evans' theory proceeds from the occurrence of mechanical defects in an oxide film. The formation of bubbles in oxide films has been observed many times. The reason for the formation of bubbles is shearing compression stresses which are created in the oxide film when the volume of the oxide formed on the metal is greater than that of the metal used $/$in forming the oxide$/$. If fissures appear on the walls of the bubbles $/$or blisters$/$, then oxygen may freely penetrate to the metal surface. In this $/$latter$/$ case, oxidation according to a linear function is possible. If the fissures are not large enough for oxygen to pass through them, or if they are not formed at all, then film growth is determined by the diffusion of ions through the film. The occurrence of bubbles on the oxide film decreases the effective cross-sectional area for diffusion, because diffusion over the empty space within a bubble is impossible. Evans considers that bubbles may be formed in all layers of an oxide film and gradually cover all parts of the metal surface. The diffusional flow of ions would decrease and, subsequently, the oxidation rate. If the probability of locating the height of bubbles inside an element of an oxide film of thickness (of the element) dx is indicated by k • dx, then the probability of the complete absence of bubbles in all film thicknesses Δx is $e^{-kd \cdot x}$ (provided that k does not depend on the thickness of the film). Then the equation for the rate of growth of the oxide film is as follows:

$$dx/dt = const \cdot e^{-kdx} \tag{3}$$

After its integration, we derive an expression for the thickness of the oxide film in dependence upon time t:

$$x = k \cdot \log (at + b), \tag{4}$$

where k, a, and b are constants.

Thus, from Evans' theory it follows a stressed state of the oxide film is not always harmful, and at a certain magnitude of stress a coating may acquire protective properties.

A. A. Smirnov /98/ theoretically studied the oxidation process of binary alloys at high temperature, using simplified alloy models which represented a continuous series of solid solutions of metals A and B. He accepted the following basic premises:

1. Only one oxide form, $M_r O_m$, is formed on an alloy, in which case, at points of metal atoms in the oxide lattice atoms A and B may be found in any ratios.

2. The concentrations of atoms A and B directly under the oxide film are constant.

3. Growth of the oxide film takes place solely by the diffusion of the metal, in which case, only those atoms may diffuse which do not go into the oxide lattice. The exchange of places between atoms of the metals which constitute the oxide lattice and those dissolved in the oxide (excess atoms in a stoichiometric sense) is impossible. Thus, the relationship of the number of A and B atoms in the lattice of an oxide layer newly forming on the surface of an oxide film depends on the relationship of the diffusional flows of stoichiometrically excess atoms.

4. The coefficients of the diffusion of A and B atoms depend on the composition of the oxide, and subsequently, may change with a growth in film thickness.

5. The energy of transference of A and B atoms into the "dissolved-in-the-alloy state" varies linearly with their concentrations.

6. An oxide film forms on the alloy, the former being compact, nonvolatile, and strongly adhesive to the film; and having no bubbles, pores or fissures. The rate of oxide film growth dx_0/dt at a given time t is determined from the expression

$$dx_0/dt = (\Gamma_A + \Gamma_B) \cdot W, \tag{5}$$

where W is the average volume of oxide recovered from one atom of metal; Γ_A and Γ_B are the diffusional flows of metals A and B which equal respectively:

$$\Gamma_A = D_A \frac{dn'_A}{dx}, \Gamma_B = D_B \frac{dn'_B}{dx},$$

where n'_A and n'_B are the absolute concentrations of stoichiometrically excessive (dissolved in the oxide) atoms A and B; and D_A and D_B are the coefficients of the diffusion of these atoms in the oxide. It is apparent from this that the compositions of oxides in different layers must be determined in order to determine oxidation rate, which presents a difficult problem even with a given, highly schematic model. Within the framework of this model one might expect the formation of a protective oxide film layer when, during a growth in film thickness, the flow of one of the metals

(Γ_B) becomes small in comparison with the flow of the other metal (Γ_A). Then an almost pure oxide layer (A_rO_m) should be formed from one of the metals. For this purpose, it is necessary for the second metal (the additive) to be greater than the critical value for every case of a value C_* -- the critical concentration. If this condition is fulfilled, and if, in the oxide layer of composition A_rO_m being formed on the surface of the oxide film, the coefficient of diffusion of both metals A and B is rather small, then oxide film growth is greatly retarded.

P. D. Dankov [40] has proposed a theory of the oxidation of 80% Ni + 20% Cr alloys based on the experimental results of E. A. Gulbransen and J. Hicman [1, 2], and also, on the results of the authors' experiments and on the main points of Smirnov's oxidation theory. However, Dankov, in accordance with existing theories on the chemical nature of solid solutions, replaced Smirnov's hypothesis, that excess particles of two metals making up oxide solutions do not interact with the stoichiometric components of a solid solution of oxides and do not interchange with metallic particles, with the hypothesis that the nature of stoichiometrically excess particles does not differ from that of the corresponding components of a stoichiometric complex. In Dankov's opinion, during the first moments of oxidation the film forming on an 80% Ni + 20% Cr alloy must nearly be analogous in composition to the alloy, and subsequently, the oxide film consists of a mixture of the oxides $NiCr_2O_4$ and NiO. After the first layers of the oxide film are formed, further oxidation is accomplished by the diffusion of metallic particles through the oxide film to its outer boundary. The relative diffusion rates of two metals depend upon the thickness of the film, as shown by Fik's equation. In the case of a Ni-Cr alloy, the mathematical expressions for the diffusional flows of Ni and Cr through the oxide film will have the following form:

$$m_{Ni} = D_{Ni} \frac{dn'_{Ni}}{dx} \approx D_{Ni} \frac{n'_{Ni}}{x} , \tag{6}$$

$$m_{Cr} = D_{Cr} \frac{dn'_{Cr}}{dx} \approx D_{Cr} \frac{n'_{Cr}}{x} \tag{7}$$

where D_{Ni} and D_{Cr} are the diffusion coefficients of Ni and Cr, n'_{Ni} and n'_{Cr} are the concentrations of stoichiometrically excess Ni and Cr particles at the alloy-oxide boundary, and x is the thickness of the oxide film.

It is apparent from these expressions that, at any inequality value $D_{Cr} > D_{Ni}$ with a sufficiently low thickness of the oxide film and the condition that $n_{Cr} < n_{Ni}$, the diffusion rate of Cr will be less than that of Ni. Under these conditions mainly nickel will be oxidized. The nickel oxide forming will be separated to the outer

surface of the oxide film and, as a result, a two-layer oxide film
of $NiCr_2O_4$ + NiO is formed. In the case of a thicker film formed
at higher temperature, the concentration gradient becomes small in
comparison with the diffusion coefficient in view of the great im-
portance of the value x. Since $D_{Cr} > D_{Ni}$, the diffusion rate of
Cr will be greater than that of Ni under these conditions. The
oxide film will be enriched with chromium oxide, its composition
and structure changing at first to a complex oxide $NiCr_2O_4$ through-
out, then to a two-layer oxide film of $NiCr_2O_4$ + Cr_2O_3. The pre-
dicted structural schemes of the oxide films are shown in Figure 32.

These schemes are based on the results of the electron dif-
fraction analysis of the surface of oxide films formed on Ni-Cr al-
loys under different condition of oxidation. The presence of an
inner layer of a surface film, which differed in structure and com-
position from the outer layer, was not proven.

The authors of the metal oxidation theories reviewed above
have considered mainly physical factors. The importance of the
chemical interaction of alloy components with the oxide film has
been pointed out by I. I. Kornilov [99].

A number of works by I. I. Kornilov and his co-workers [102,
103] deal with the study of oxidation processes of Fe-Cr-Al alloys.
Based on these studies, Kornilov has proposed three oxidation
schemes of Fe-Cr-Al alloys in the solid state independence upon the
temperature of heating. The first oxidation scheme (I) takes in
the temperature interval from room temperature up to 800°, the sec-
ond, from 800-1,200°, and the third, from 1,200° to melting point.
According to the first scheme, a solid solution of oxides of the
type (Fe, Cr, Al)$_2O_3$ with spinel structure are formed on the surface
of Fe-Cr-Al alloys. The oxidation reaction under these conditions
may be given in the following form:

$$2(Fe, Cr, Al) + 4\ 1/2\ O_2 \rightarrow Fe_2O_3 + Cr_2O_3 + Al_2O_3 \tag{I}$$
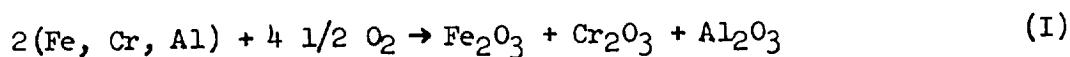
According to scheme II, along with the simultaneous oxida-
tion of all the alloy components, an aluminothermal reaction of
the reduction of Fe and Cr takes place in the surface layer of the
alloys in places where these oxides come into contact with alumi-
num atoms.

According to the second scheme, the oxidation reaction may
be given in the following form:

$$2(Fe, Cr, Al) + 4\ 1/2\ O_2 \rightarrow Fe_2O_3 + Cr_2O_3 + Al_2O_3,$$

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3, \tag{II}$$

$$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3.$$
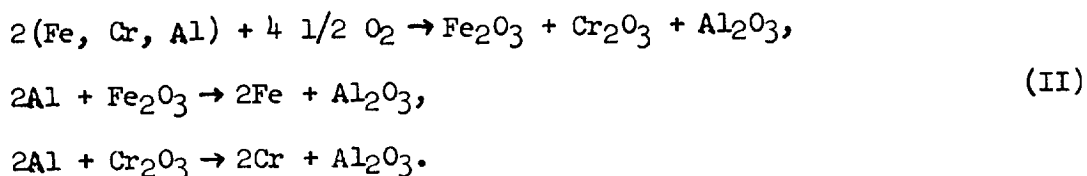
A solid solution of all three oxides $(Fe, Cr, Al)_2O_3 + Al_2O_3$ is formed on the alloy surface.

Upon oxidation by the third scheme, aluminothermal reactions and Al diffusion take place at a considerable rate. During the oxidation process mainly aluminum oxide is formed on the alloy surface.

I. I. Kornilov discovered that the concentration of Al in the surface layer of the alloy decreased during the oxidation of Fe-Cr-Al alloys. The higher the Al concentration in the alloy the lesser its decrease in concentration during the oxidation process.

I. N. Frantsevich /104/ regards the formation of protective films on metals at high temperatures as a purely electrochemical process. He predicts that the oxide film plays the role of an electrolyte in the system "metal-protective film-gaseous oxidizing medium," in which case, electricity is only conducted by those ions which, due to fluctuation, are in an inter-lattice position, or by those ions which surround a vacant point; the metal acts as anode; and oxygen adsorbed on the surface of the oxide film, as cathode. Points where pores and fissure appear in the oxide film, the former developing throughout the process of film formation, fulfill the role of an external circuit which closes this galvanic cell; because an oxide film forming on the uncoated parts of a metal shows an electron productivity even at thicknesses of 30-50 Å (Figure 33).

Then the rate of oxide film formation is determined by the relationship

$$\frac{dx}{dt} = \frac{(E_K - E_A - P)f}{\zeta + R},$$

(8)

where E_K and E_A are the cathode and anode potentials; P is the degree of polarization; ζ and R are the internal and external resistances in the circuit of the galvanic cell; and $f = M/ZF$ (M is the mole. wt. of the metal; Z, the valence; and F, Faraday's number).

If the weight of the forming film relates to unit surface area, equation (8) takes on the form:

$$\frac{dx}{dt} = \frac{(E_K - E_A - P)f}{\zeta_0 \cdot \frac{x}{d} + R},$$

(9)

where ζ_0 is the specific resistance of the oxide; and d, the density of the oxide. After integration the equation appears as

$$\frac{\zeta_0}{d} x^2 + Rx = (E_K - E_A - P)ft + C'.$$

(10)

In equation (10) the coefficients of x^2 and x characterize the properties of the oxide film, in which case, Frantsevich considers that R (the electrical resistance of extremely thin oxide layers forming on the uncoated parts of the metal with continuously developing (new) pores and fissures) will be constant over a wide interval of time. The coefficient of t characterizes the properties of the oxidized metal, namely, its affinity for oxygen.

From equation (10) it follows that the higher the electrical conductivity and density of the oxide, the weaker its protective effect. However, the resistance of metals and alloys to oxidation is determined not only by the protective properties of oxide films but also by the volatility of alloy components (or the metal itself). By bringing about the minimum value of (E_K - E_A - P), the heat-resistance of an alloy may be sharply increased, if its lattice is stabilized.

In concluding this section, let us briefly consider the possibility of using the above-mentioned theories in considering the oxidation mechanism of Ni-Cr alloys. First of all, let us state that there is no comprehensive theory of the oxidation of alloys which will explain the results obtained by the authors of this book and other authors.

The theories of the oxidation of pure metals propounded by Wagner and Mott /95/ cannot be used to explain the oxidation mechanism of multi-component alloys because the theory does not consider the changing compositions of oxide films in dependence upon temperature and film thickness. These theories of metal oxidation treat the oxidation process as a purely diffusional process; they do not consider secondary reactions or phase transformations in oxide films.

Hauffe's theory of the oxidation of alloys in some cases gives a qualitative explanation for the influence of small amounts of additives on the oxidation rate of binary alloys. However, the theory does not permit a complete explanation for the dependence of the oxidation rate of multi-component alloys on the concentration and valence of alloying components.

The fallaciousness of the initial premises of the alloy oxidation theory of A. A. Smirnov was shown by P. D. Dankov /36/. Smirnov, in his theory which considered that the coating on a two-component alloy consisted of oxides which formed a solid solution, concluded that the formation, on the outer surface of a coating, of a high concentration of the oxide of some component (in comparison with its concentration on the inner surface of the coating) was possible. With such a distribution of oxides, a concentration gradient of one of the metals, directed from the coating-gas to the alloy-coating boundary, develops -- which contradicts the principles of thermodynamics. Significant differences in the concentration of metals and oxygen in a coating on alloys may arise in those cases when the coating consists of different phase-bounded layers.

Other initial positions of Smirnov's theory are erroneous; for instance, the composition of an alloy does not change at the alloy-coating boundary. As shown in the authors' work, the composition of oxide films does not correspond to that of the alloy because the composition of the alloy layer adjoining the coating cannot remain constant.

Besides this, it was experimentally established in work /106/ that there was considerable aluminum and titanium impoverishment at a depth of 30 microns from the alloy-oxide film boundary in a layer of a sample nichrome alloy containing 2.4% Al and 1.5% Ti after heating 300 hours at 700-900°.

The basic proposition of Evans' theory of the effect of bubbles in a coating on its oxidation kinetics is limited to a particular case and cannot be used to explain the oxidation mechanism of Ni-Cr alloys when no bubbles are observed in the coating.

In the electrochemical theory of Frantsevich, an extremely large role is assigned to pores and fissures in the formation and growth of an oxide film, the former, according to his assumption, being formed continuously during the oxidation process.

Frantsevich's conclusion as to the protective properties of oxide films is erroneous also. On the basis of his theory, he reaches the following conclusion: The more electroconductive an oxide layer, the higher its density and the lesser its protective effect. To prove this, Frantsevich uses films consisting of oxides of aluminum, silicon, and beryllium as examples of protective films.

However, it is well known that these oxide films do not protect "their own" metals from oxidation, beginning with some temperature characteristic for a given metal. For example, an oxide film on aluminum only protects it from oxidation up to 500°. Beginning at 500°, it oxidizes according to a linear function, as Gulbransen has shown. At 1,000° in vacuo, aluminum vaporizes through the oxide film at a rapid rate (W = 8 · 10⁻⁵ g/cm² sec). But this same film formed on iron, for example, protects it from oxidation up to 950-1,000°.

With a growth in the density of aluminum oxide from 2.8 up to 4 g/cm³, the protective properties of oxide films will improve. The protective properties of a coating depend, to a considerably higher degree than upon density, upon crystal structure, melting point, the dissociation and volatility of oxides, and also, upon the fact that the oxides in the film form among themselves (solid solutions, chemical compounds or mixtures).

The theories of high temperature oxidation of Arkharov (mainly for steel), Kornilov (Ni-Cr-Al alloys) and Dankov (80% Ni + 20% Cr alloys), although they are qualitative, explain more deeply and fully the oxidation mechanism of alloys in the first three quantitative theories (Wagner-Hauffe, Evans, and Frantsevich).

The basic conclusion of Arkharov's theory /17/, which follows from his theory of the oxidation of alloyed steels, that the

protective properties of oxide films consisting of spinel increase
with decreases in their lattice constant, has found confirmation
in the case of the oxidation of both Fe-Cr-Al and Ni-Cr-Al alloys.

Actually, adding 8-10% of Al to both iron- and chromium-
base and also nickel and chromium alloys increases their heat-
resistance considerably because oxide films consisting of solid
solutions of spinels of the types $FeCr_2O_4$ and $FeAl_2O_4$ (for iron-
and chromium-base alloys) and $NiCr_2O_4$ and $NiAl_2O_4$ (for nickel- and
chromium-base alloys) form on their surfaces.

At 900-1,000° films consisting of oxides of spinel structure
with smaller lattice constant form on these alloys: $FeAl_2O_4$
(α = 8.12 Å), $NiAl_2O_4$ (α = 8.05 Å), and γ = Al_2O_3 (α = 7.89 Å).

Also confirmed were the main conclusions of Kornilov's theory
regarding the nature of secondary oxidation and reduction reactions
in a coating and their effect on the rate of growth and mechanism
of the formation of oxide films.

The ideas and conclusions from Dankov's theory on the differ-
ent role of the concentration gradient and the coefficient of dif-
fusion of individual alloy components in the oxidation process in
the first and later stages of film growth have been fully substan-
tiated. The use of these conclusions to explain the oxidation
mechanism of 80% Ni + 20% Cr alloys will be considered below.

For the sake of brevity, the last three qualitative theories
will be called crystallochemical, because they view the oxidation
process as such, in contrast to the theories of Wagner-Hauffe and
Frantsevich, which regard this process as electrochemical -- and
will be called thusly.

A general and substantial defect of the crystallochemical
and electrochemical theories is that, in considering the oxidation
mechanism of alloys (solid solutions) and the effect of alloying
elements in alloys on the oxidation rate of the latter, they do
not take into account the fact that alloying elements, by increas-
ing the bond energy between the atoms in the crystal lattice of an
alloy, increase the energy of the transfer of ions from the lat-
tice of the alloy to that of the oxides in the coating. The con-
centration of individual components at the alloy-coating boundary
is determined by their activities, the numerical values of which
will depend upon the nature of the solid solution.

With increase in temperature and oxidation time the state
of a solid solution (alloy) changes. The bond energies in the
crystal lattice and the activity of its components, and, subse-
quently, the concentration of the latter on the alloy-coating bound-
ary, change in dependence upon the state of the alloy. The concen-
trations, size of the ions, and the heats of formation of oxides of
alloy components will determine the composition of the coating.
The protective properties of an oxide film depend, first of all,
upon the crystallochemical nature of the oxides and upon whether

single-phase chemical compounds (of the type of spinels $NiAl_2O_4$ or $FeAl_2O_4$, etc.) and their solid solutions or mixtures are formed from the oxides of the alloy components in the coating. Along with this, other factors, for example, the volatility of oxides which create pores in a coating (MoO_3, B_2O_3, WO_3); shearing stresses which weaken the film and cause fissures to form; and the melting points of oxides of some of the alloy components (for example, V_2O_5, B_2O_3) have an essential effect on the protective properties of a coating.

After those comments relative to the important theories on the oxidation of metals and alloys, and also, on the nature of the oxidation process (see Chapter I), the authors shall review the results of experiments on the oxidizability of nichrome alloys and attempt to explain them on the basis of their own ideas, expressed in those comments and theories discussed above. First of all, we are analyzing the results of our own investigations because the structural and kinetic studies were carried out at the same values of temperature and heating time. Furthermore, qualitative electronographic (electron diffraction) analysis of the phase composition of a coating with respect to its thickness was carried out in our studies.

An essential shortcoming of studies of the oxidation process of nichrome alloys by other authors is that they either do not consider the chemical and phase analysis of a coating, determining the service life of these alloys only in dependence upon additives of some alloying elements (Hessenbruch), or, the phase composition of a coating is determined for short periods of time (1-60 min) and for temperatures of $400-950°$; but service life has been determined for 25, 86 and 175 hours at $1,175°$ (Gulbransen).

Upon turning to the analysis and explanation of the results of studies on the oxidizability of 80% Ni + 20% Cr and Ni-Cr alloys containing additives of Al, Ti, B and other elements, it should be noted first of all that the chemical composition of oxides in a coating on the stated alloys does not correspond to that of the alloys and changes substantially in dependence upon temperature and heating time. This is one of the main experimental facts which attests, more so than anything else, to the fact that the oxidation process in the given case takes place mainly as a result of the diffusion of metal ions from the alloy-oxide film boundary to the oxide film-gaseous medium boundary. If an oxide film should grow on the surface of an alloy as the result of the diffusion of oxygen, then the composition of oxides in the inner surface would not essentially change in dependence upon temperature and heating time.

Another experimental fact is that, along with simple oxides of alloy components, oxides of complex composition, i.e., chemical compounds of the spinel type and their solid solutions, were discovered on the surface of the Ni-Cr alloys studied, in which case,

their chemical compositions differed in dependence upon their location depthwise in the coating. This fact shows that the oxidation process of alloys includes secondary oxidation and reduction reactions which take place in the coating. Thus, the oxidation mechanism of alloys of given composition will be determined by the following basic factors:

1) the thermodynamic activities of the alloy components;

2) parameters of the diffusion of ions of alloy components;

3) rates of the chemical reactions which take place in the film and on its surface; and

4) the crystallochemical nature of the coating.

The thermodynamic activities of Ni-Cr alloy components, unfortunately, have not been determined. Work in this direction have only just begun in our laboratory. The first experiments in determining the vaporization rates of Ni-Cr-Ti alloy components, carried out by D. V. Ignatov, showed good correspondence between the vaporization rates of Ni-Cr-Ti alloy components and the oxidation rates of these alloys in dependence upon Ti concentration.

To qualitatively evaluate the degree of activity of alloy components, data on the <u>in vacuo</u> vaporization rates of pure metals (alloy components) may be used. Although these conditions are not analogous to a case of the formation of free ions at the alloy-oxide boundary, these thermodynamic characteristics must nonetheless, to some measure, be effected and affect the creation of concentrations of ions of some alloy component at the stated boundary. The concentration gradient of these ions and their dimensions, and also the thermodynamic properties and structure of the oxide film, will determine their diffusion rate through the film.

On the basis of these assumptions, the authors considered it possible to use data on the vaporization rates of component metals of nichrome alloys for explaining the changes in the chemical composition of oxide films on alloys of given composition in dependence upon temperature.

Besides this, the authors have also used thermodynamic data on the energies of formation of oxides of alloy components to explain certain chemical reactions which occur in a coating during oxidation.

Sizes of the radii of ions are given in Table 14.

<div align="center">

TABLE 14

SIZES OF RADII OF IONS [105]

</div>

Ion	Ion Radius, $\overset{\circ}{A}$	Ion	Ion Radius, $\overset{\circ}{A}$
Ni^{2+}	0.74	Ti^{4+}	0.64
Cr^{3+}	0.64	B^{3+}	0.20
Al^{3+}	0.57	O^{2-}	1.36

Thermodynamic data on metals and oxides are given in Tables 15 and 16.

Finally, in order to explain the oxidation rate of different alloys, we have also used the phase composition of alloys.

As P. D. Dankov has shown /40/, the diffusion rate of ions of different alloy components in an oxide film may change in dependence upon film thickness. A low thickness of the oxide film, i.e., at low resistance to the motion of diffusing particles, their rate of transfer is determined by the concentration of free ions at the alloy-oxide boundary. At considerable film thickness, i.e., at high resistance to the motion of diffusing particles, the coefficient of diffusion will have decisive value. Assuming that the concentration of free ions of a given component at the alloy-coating boundary is proportional to its concentration in the alloys, and that the coefficient of the diffusion of Cr is greater than that of Ni, Dankov attributes the change in composition and structure of the oxide film on an 80% Ni + 20% Cr alloy (in dependence upon oxidation temperature) only to film thickness. If his assumption is correct, then at any temperature very thin films on a Ni-Cr alloy must consist of nickel oxide. To prove this assumption the authors heated 80% Ni + 20% Cr alloy samples at 700° for several minutes. Electron diffraction patterns from these samples showed that nickel oxide NiO actually does develop on the surface of the alloy after 1-3 min at 700°; after 5-6 min, a chemical compound of nickel and chromium oxides, $NiCr_2O_4$; and after 10-12 min, chromium oxide $\propto = Cr_2O_3$. Subsequently, the above-mentioned supposition of Dankov was confirmed. However, the occurrence of an oxide of the composition $NiCr_2O_4$ on the surface of an 80% Ni-20% Cr alloy at 800-1,000°, i.e., under conditions when the thickness of the film is higher than it is at 500-700°, cannot be explained without taking into consideration the change in the rate of formation of free ions ("stoichiometrically excess particles") in dependence upon temperature.

At 800-1,000° the formation rate of free nickel ions (as shown in Table 15) increases, which results in an increase in the diffusional flow of nickel ions in the oxide film. Besides this, an increase in nickel ion concentration at the alloy-coating boundary with the course of time (i.e., with increasing thickness of the coating) will take place as a result of Cr impoverishment in the alloy layer adjoining this boundary; in which case, this process is accelerated as the temperature increases.

From the results of the present work and those given in Tables 15 and 16 on the thermodynamic properties of metals and alloys, the stated order of development of different oxides on the surface of an 80% Ni + 20% Cr alloy may be explained in the following way:

TABLE 15

VAPORIZATION RATES OF METALS IN VACUO [114]

Metal	P¹), mk	10^{-2}	10^{-1}	1	10	100	1,000	mp, °K³)	P at mp, mk⁴)	Vaporization Energy, cal
B	t, °C	1,052	1,140	1,239	1,355	1,489	1,648	2,000-2,800		
	W²), g/cm²·sec	5.27×10^{-8}	5.11×10^{-7}	4.94×10^{-6}	4.76×10^{-5}	4.57×10^{-4}	4.38×10^{-3}			
Al	t, °C	724	808	889	996	1,123	1,274	600	1.2×10^{-3}	69.62
	W, g/cm²·sec	9.6×10^{-8}	9.21×10^{-7}	8.88×10^{-6}	8.51×10^{-5}	8.11×10^{-4}	7.69×10^{-3}			
Ti	t, °C	1,134	1,249	1,384	1,546	1,742	1,965	1,727	84.3	112.76
	W, g/cm²·sec	1.08×10^{-7}	1.04×10^{-6}	9.92×10^{-6}	9.47×10^{-5}	9.00×10^{-4}	8.53×10^{-3}			
Cr	t, °C	907	992	1,090	1,205	1,342	1,504	1,900	6.35×10^{-4}	69.6
	W, g/cm²·sec	1.22×10^{-7}	1.18×10^{-6}	1.14×10^{-5}	1.09×10^{-4}	1.05×10^{-3}	1.00×10^{-2}			
Ni	t, °C	1,157	1,257	1,371	1,510	1,679	1,884	1,455	4.37	82.2
	W, g/cm²·sec	1.18×10^{-7}	1.14×10^{-6}	1.10×10^{-5}	1.06×10^{-4}	1.01×10^{-3}	9.62×10^{-3}			

1) P -- vapor pressure; 2) W -- vaporization rate; 3) mp -- melting point, °K; 4) vapor pressure at melting point, mk [milligram calories ?]

TABLE 16

THERMODYNAMIC AND PHYSICAL PROPERTIES OF OXIDES [115]

Oxide				Vaporization Temperature, °K	
				10^{-3} atm	1 atm
$1/3Al_2O_3$	- 126.0	- 133.4 ± 0.1	- 24.8	2,300 ± 20	Decomposes, 2,740 ± 60	Decomposes, 3,800 ± 200
$1/2TiO_2$	- 106.2	- 112.8 ± 0.1	- 22.1	2,128 ± 20		Decomposes, 3,200 ± 300
$1/3B_2O_3$	- 96	- 101.8 ± 1	- 21.3	723	1,740	2,520
$1/3Cr_2O_3$	- 83.5	- 90.0 ± 0.3	- 21.8	2,710 ± 10		Decomposes, 3,300 ± 300
NiO	- 51.3	- 58.0 ± 0.5	- 22.4	2,230 ± 20		
$1/2CeO_2$	- 116	- 122.5 ± 2	- 22	3,000 ± 20 under O_2 pressure		
$1/3La_2O_3$	- 138.5	- 145 ± 1	- 22	2,590 ± 20		4,470 ± 300
$1/2CaO$	- 144.3	- 151.7 ± 0.5	- 25	2,860 ± 25	2,650 ± 50	3,800 ± 200
$1/2ThO_2$	- 140	- 146.6 ± 0.5	- 21	3,225 ± 200		4,670 ± 300
$1/2SiO_2$	- 98.5	- 105.1 ± 1	- 21.8	1,973	Decomposes, 2,250 ± 50	
$1/3MoO_3$	- 54.0	- 60.1 ± 0.5	- 20.5	1,068	1,055 ± 10	1,530 ± 50
$1/5Nb_2O_5$	- 84.4	- 91.0 ± 0.1	- 22	1,733 ± 5		--

In the first stage of oxidation, i.e., at first contact between a clean alloy surface and air, the composition of the forming oxide film, apparently, must correspond to that of the alloy. After formation of the first oxide layer, further oxidation is connected with the necessity of metallic particles penetrating the oxide film. In this stage, the nature of oxidation is determined by diffusion factors, which include activation energies and the coefficient of the diffusion of metal ions and their concentration gradient in the oxide coating.

At 400°, when oxide film thickness is negligible, and the flow of particles of one of the components seems predominant, the concentration of free ions of this component is higher at the alloy-coating boundary. In the given case, mostly nickel diffuses through the oxide film and therefore, the oxide NiO develops on the surface of the initial oxide film.

The importance of the coefficient and activation energy of diffusion increases with film thickness. In the case under consideration, i.e., the oxidation of an 80% Ni + 20% Cr alloy at 500-700°, Cr more easily diffuses through the oxide film. This may be explained by the fact that, as a result of the high rate of Cr ion formation (the vaporization rate of Cr at 900-1,000° is 100 times that of Ni) their concentration at the alloy-coating boundary, with increases in temperature, is greater than that of Ni ions. Also, the radius of the Cr ion is less than that of Ni by 0.10 $\overset{o}{A}$ (see Table 14). Therefore, the diffusion rate of Cr will exceed that of Ni under the given conditions. In this connection we may predict that at 500-700° the formation of an oxide film on a Ni-Cr alloy will take place in three stages:

1) analogously to the oxidation process at 400°, nickel oxide NiO is formed on the alloy surface;

2) when the oxide film reaches a certain thickness, the diffusion of Ni and Cr reaches a point where there are two Cr^{3+} ions to each Ni^{2+} ion; which results in the formation of an oxide film on the alloy surface, the latter consisting of oxides of nickel and chromium or their chemical compound, $NiCr_2O_4$;

3) with further increases in oxide film thickness the diffusion of Cr becomes predominant and chromium oxide Cr_2O_3 forms on the surface of the oxide film. Hereupon, the nickel oxide formed earlier in the inner layers of the oxide film are reduced by Cr to metallic Ni according to the reaction

$$3NiO + 2Cr \rightarrow Cr_2O_3 + 2Ni.$$
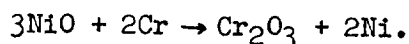
As shown in Table 15, the free energy of nickel oxide formation is 51.3 kcal/gram-atom, but that of chromium oxide Cr_2O_3 is 83.5 cal/gram-atom. Therefore, such a reaction is, thermodynamically, entirely possible, and it is accomplished at 600-1,000° with comparative ease. The remaining nickel is distributed in the alloy and the

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oxide film in proportion to its solubilities in them, i.e., its solubility in the alloy and in the film. The oxide film on an 80% Ni + 20% Cr alloy at 500-700° after sufficient oxidation time (10-12 min) consists mainly of chromium oxide throughout.

As Table 4 shows, at 800-1,000° the diffusion rate of Cr practically doubles that of Ni, which explains the intensive formation of free nickel ions at these temperatures. This results in increased Ni concentration at the alloy-coating boundary. The formation of an oxide film under these conditions also takes place in three stages:

1) a thin layer of nickel oxide NiO forms on the alloy surface;

2) at a certain oxide film thickness, chromium, along with nickel, begins to diffuse and the composition of the oxide film changes -- the film consists of $NiCr_2O_4$;

3) due to the lack of oxygen in the inner layers of the oxide film, nickel oxide $NiCr_2O_4$ is reduced by chromium.

In this way, a two-layer oxide film is formed on the surface of an 80% Ni + 20% Cr alloy, the inner layer consisting of chromium oxide $\alpha = Cr_2O_3$ and the outer layer, of oxide $NiCr_2O_4$.

The intensive internal oxidation of this alloy is also explained by the selective oxidation of chromium by the oxygen in the nickel oxide.

Since the thickness of the $NiCr_2O_4$ layer in an oxide film increases with temperature, and that of the $\alpha = Cr_2O_3$ layer decreases, it follows that oxygen diffuses along with the metal during the oxidation of an 80% Ni + 20% Cr alloy. The rate of diffusion of oxygen through the film increases with temperature. At 800° the concentration of oxygen at a short distance from the inner surface of the oxide film has already been so lowered that $NiCr_2O_4$ is reduced by Cr ions diffusing through the film from the alloy. At 1,000° nickel oxide $NiCr_2O_4$ can exist almost /entirely/ at the alloy-coating boundary itself. Subsequently, considerable diffusion of oxygen inside the oxide film takes place at this temperature.

From this statement it follows that, besides the diffusion of Ni and Cr, in the oxide film on an 80% Ni + 20% Cr alloy, other processes take place: oxygen diffusion, oxidation-reduction exchange reactions, formation and decomposition of a chemical compound of nickel and chromium oxides and structural transformations connected with this process. The surface area covered by the oxide film changes during the oxidation process. The composition of the alloy, especially its surface layer directly under the oxide film, also changes; and, if the composition of the oxide films is considered, the alloy is impoverished of chromium. But this may then change the energy of formation of free ions of alloy components and, subsequently, affect the diffusion rate of metals in the oxide film. However, the parabolic shape of the "weight increase - time" curves at 900-1,000° shows that, regardless of the presence of

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several simultaneously occurring processes, the oxidation rate at these temperatures and the length of endurance are determined by the rate of diffusion of the reagents through the oxide film, i.e., the slowest stage of the oxidation process of an 80% Ni + 20% Cr alloy under these conditions is the diffusion of reaction components through the oxide film.

As the results of the authors' investigations show, at 800-1,000° the oxidation rate of an 80% Ni + 20% Cr alloy is lower than that of Cr, in which case, the difference in the oxidation rate of the alloy and Cr increases the temperature (see Figure 8). In comparing the change in the relationship of the oxidation rates of Cr and the alloy, and also, the structure and composition of oxide films on their surfaces at corresponding temperatures, it follows that oxide $NiCr_2O_4$ is more protective at 800-1,000° than chromium oxide α - Cr_2O_3. This may be explained by the fact that the coefficient of diffusion and the activation energy of the diffusion of Cr through the chromium oxide lattice differ from the corresponding values for the diffusion of Cr through the lattice of spinel-type oxide $NiCr_2O_4$.

The results of experiments expressly for determining the parameters of the diffusion of Cr in the oxide $NiCr_2O_4$ and α = Cr_2O_3 /54/ are given in Table 17.

TABLE 17

PARAMETERS OF THE DIFFUSION OF Cr IN OXIDES

System	Q, cal/mole	D/cm² sec at 900°	D at 1,000°
Cr in α - Cr_2O_3	22,000	$7.9 \cdot 10^{-12}$	$1.37 \cdot 10^{-11}$
Cr in $NiCr_2O_4$	44,800	$3.99 \cdot 10^{-13}$	$1.88 \cdot 10^{-12}$

Thus, the many years of controversy among scientists concerning which of the oxides, α - Cr_2O_3 or $NiCr_2O_4$, is protective on a Ni-Cr alloy may be considered as solved. In the temperature range of 500-700° the protective oxide film on an 80% Ni + 20% Cr alloy consists of α - Cr_2O_3, and in the temperature range of 800-1,000° it consists of oxide $NiCr_2O_4$.

Dankov's proposed mechanism of the oxidation of a binary 80% Ni + 20% Cr alloy is not confirmed by the layer composition of oxide films. The reason for this consists in the fact that Dankov's theory does not consider the limited solubility of NiO and α - Cr_2O_3 oxides in the oxide $NiCr_2O_4$ /89/, and also, the possibility of the reduction of nickel oxide in the inner layers of the oxide film and the diffusion of oxygen in the oxide film.

In conclusion, it should be mentioned that the oxidation of an 80% Ni + 20% Cr alloy at 600-1,000° takes place mainly due to

the diffusion of chromium ions. Even at 1,000°, if the composition of the oxide film $NiCr_2O_4$ is considered, there are two chromium ions for each nickel ion.

This fact, as we have pointed out, is explainable if one considers thermodynamic data on Ni and Cr and their oxides.

The <u>in vacuo</u> vaporization rate of Ni is almost 100 times less than that of Cr. The size of the Ni^{2+} ion is also larger than that of Cr^{3+}. Therefore, at the same temperature and composition of the oxide film, the diffusion rate of chromium will be higher than that of nickel. The low oxidation rate of Ni-Cr alloys in comparison with that of pure Cr may be explained by the fact that, during oxidation of the alloy, Cr ions, after some time and in dependence upon temperature, come to the alloy-oxide boundary from deep layers of the alloy, diffusing through the lattice of a Cr impoverished alloy layer.

In a case of chromium oxidation, Cr ions transfer directly from the metal lattice to the oxide lattice.

Thus, the oxidation mechanism of alloys differs in general principle from that of pure metals, not only because chemical reactions take place between the components of an alloy but also because, in an alloy, the ions of some component diffusing toward the coating-gas boundary must overcome the bond energies in the lattice of the alloy when diffusing from its deeper layers.

Turning to the results of the analysis of the ternary alloy Ni-Cr-Al, the authors' shall first review thermodynamic data on this alloy and its oxides.

As shown in Table 15, the vaporization rate of Al exceeds that of Cr by 70-80 times in the temperature range of 900-1,200°.

The ion radius of Al^{3+} is 0.57 Å, i.e., 0.07 Å less than that of Cr, and 0.17 Å less than that of Ni. At 700-1,000° an oxide film consisting of the oxide $\gamma = Al_2O_3$ is formed on Al.

It is known that the oxide lattice of $\gamma = Al_2O_3$ is a dense, cubic packing of oxygen O^{-2} ions, the former having octahedral voids ~1 Å in size and tetrahedral voids ~ 0.44 Å in size. In this lattice, 21 1/3 Al^{3+} ions are distributed statistically over 24 voids /107.

As the authors' experiments and those of other authors on the oxidation of pure aluminum, upon heating Al in the temperature range of 600-1,000°, Al ions easily pass through the $\gamma = Al_2O_3$ lattice, because the oxidation rate in this temperature range corresponds to a linear function of oxidation. Thus, an oxide film consisting of $\gamma = Al_2O_3$ on aluminum does not protect it in this temperature range. This is explained by the fact that, on one hand, there are many voids in the $\gamma = Al_2O_3$ lattice which are nearly equal in size to the Al ion; and on the other hand, by the low energy and high rate of vaporization of Al after melting point.

Thus, it is entirely logical to expect that the thermodynamic activity of Al in the alloy will exceed that of Cr. However,

an oxide film of $\gamma = Al_2O_3$ will have better protective properties for the alloy than films consisting of NiO and Cr_2O_3. Lattices of the oxides NiO and Cr_2O_3 have vacant cation points along which Ni and Cr ions diffuse with comparative ease in the temperature range of 800-1,000°.

The lattice of oxide $\gamma = Al_2O_3$ contains only interstitial voids, the largest of which are ~ 1 Å. Therefore, the passage of Ni and Cr ions (having diameters of 1.48 and 1.28 Å respectively) through the lattice of oxide $\gamma = Al_2O_3$ requires more activation energy for diffusion than in the case of the movement of ions of the stated metals through the lattices of oxides NiO and Cr_2O_3.

From Figure 14 we see first of all that the oxidation rate of Ni-Cr alloys is substantially lowered by the addition of Al in amounts of 4.18 and 7.22%, in which case, the composition and structure of films forming on the alloys at 900-1,000° correspond either to a solid solution of spinels $NiCr_2O_4$ and $NiAl_2O_4$ predominant, or to spinel [sic!] $\gamma = Al_2O_3$. Such a composition of oxides shows that the thermodynamic activity of Al in the alloy is greater than that of Cr.

In this connection, the oxidation of Ni-Cr-Al alloys and the growth of a coating on them is enhanced by the loss of Al from the alloy. Since more Al ions form at the alloy-coating boundary than Ni or Cr ions, and the heat of formation of aluminum oxide ($1/3 Al_2O_3$ -- 133 cal/mole) is greater than that of nickel or chromium oxide, then mainly aluminum oxide $\gamma = Al_2O_3$ is formed near this boundary.

For this same reason, and as a result of the smaller size of Al ions in comparison with the size of Ni and Cr ions, a coating consisting either of a solid solution of spinels $NiCr_2O_4$ and $NiAl_2O_4$ with $NiAl_2O_4$ predominant, or of oxide $\gamma = Al_2O_3$ is formed on the surface of the alloys. Although the lattices of spinels $NiCr_2O_4$ and $NiAl_2O_4$ have similar structures, they differ in diffusion rate, which was shown by direct experiments [54]. In the octahedral voids of the $NiCr_2O_4$ lattice, which are about 1 Å in size, there are Cr ions 1.28 Å in diameter, and in similar voids of the $NiAl_2O_4$ lattice there are Al ions 1.14 Å in diameter. Therefore, the $NiCr_2O_4$ lattice will be deformed to a large degree, and the voids in the lattice will be expanded; and also, the lattice constants of these spinels are equal: a = 8.31 Å for $NiCr_2O_4$ and a = 8.05 Å for $NiAl_2O_4$.

Thus, the role of a 4-7% addition of Al consists in the creation of protective oxide films consisting either of a solid solution of spinels $NiCr_2O_4$ and $NiAl_2O_4$, or of spinel $\gamma = Al_2O_3$.

Moreover, in agreement with works [108, 109], small additions of Al (up to 2%), when the alloy is still homogeneous and a γ-solid solution, increase the bond energy between the atoms of the alloy.

For this reason, the activation energy for the diffusion
and transfer of ions of alloy components from the alloy lattice to
the oxide lattice must be increased.

At an Al content of over 4%, when the Ni_3Al phase begins to
form and separate, the activation energy for the diffusion and trans-
fer of ions of metals from the alloy lattice to the lattice of the
oxides of the coating is still increased more so than in the case
of a solid solution. Since an oxide film develops in this phase,
the former consisting of oxides $NiAl_2O_4$ and $\gamma = Al_2O_3$, and because
it shows good properties of protection against corrosion, the pres-
ence of the Ni_3Al phase will prevent oxidation of the alloy along
the grain boundary, which is also confirmed by data from the metal-
lographic study of lateral microsections of oxidized samples of
Ni-Cr-Al alloys (see Figures 19-21).

Consequently, Al contained in the alloy at $700-1,000°$ re-
tards the diffusion and decreases the rate of transfer of metal
ions (alloy components) from the lattice of the alloy to that of
the oxides of the coating; and this also lowers the oxidation rate
of a Ni-Cr-Al alloy.

Even though many investigations of the structure of oxide
films on alloys have shown that, on the surface of alloys, coatings
are formed which consist mainly of oxides of those alloy components
whose ions have the smallest radii, and not of those components
whose oxides are thermodynamically more stable, the thermodynamic
factors, nevertheless, cannot be disregarded. The latter determine
the composition of the coating in its inner layers which border
upon the alloy surface. Under these conditions, selective oxida-
tion reactions may take place with those alloy components which
have, more so than other components, the energy to form oxides.
From the authors' investigations it follows that the composition
and structure of oxide films on the surface of Ni-Cr and Ni-Cr-Al
alloys change according to film thickness, in which case, the nearer
a given layer to the alloy-coating boundary, the higher the concen-
tration of more thermodynamically stable oxides in this layer. The
concentration of aluminum oxide in the inner layers of the oxide
film were also discovered in Fe-Al alloys $\boxed{5}$. In light of these
data, the report of Gulbransen and McMillan $\boxed{85}$ that oxide films
on Ni-Cr-Mn and Ni-Cr-Mn-Si alloys have similar composition can
hardly be considered correct. It is possible that silicon dioxide
is concentrated at the alloy-coating boundary and that this ef-
fects the higher heat-resistance of Ni-Cr-Mn-Si alloys in compari-
son with Ni-Cr-Mn alloys.

From Figure 24 it follows that, for Ni-Cr-Ti alloys oxidized
at $1,000°$, the oxidation rate has a minimum value $(3.7 \cdot 10^{-2}$
$mg/cm^2 \cdot hr)$ for alloys containing 0.68% Ti and a maximum value
$(10.4 \cdot 10^{-2} mg/cm^2 \cdot hr)$ for alloys with 9.76% of Ti added. For
intermediate values of Ti concentration in the alloy (3.44 and
5.88%) the oxidation rates are equal respectively to $5.7 \cdot 10^{-2}$

and $4.53 \cdot 10^{-2}$ mg/cm^2 · hr. Thus, from these data it is apparent that the average oxidation rates at 1,000° (after 25 hours) increase with Ti concentration in the alloy, with the exception of a concentration of 5.88%, when the oxidation rate is 6% less than when the concentration is 3.44%.

From an analysis of the data in Table 11 on the chemical composition and microstructure of an alloy with additives of Ti, it follows that, with an increase in Ti concentration, alloys of a Υ-solid solution are transformed into a two-phase system composed of a Υ-solid solution and a Mi$_3$Ti phase, wherein, the Ni$_3$Ti phase increases with Ti concentration. The Mi$_3$Ti phase itself, both according to the data of Kornilov and Pylayeva and that of the authors, is intensively oxidized even at 800°, in which case, the oxidation rate is equal to 1.1 mg/cm^2 · hr. The high oxidation rate of this phase is explained by the fact that an oxide film consisting of TiO$_2$ is formed on the sample surface from this compound (Ni$_3$Ti). Nickel oxide NiO cannot be formed in the given case because the free energy of TiO$_2$ formation is twice that of NiO formation (Table 16). According to the data of works $\underline{/3, 5/}$, the crystal lattice of rutile contains vacant anion points through which atoms (or ions) of oxygen might possibly diffuse.

For this reason, an oxide film consisting of TiO$_2$ is not protective to titanium itself or to a Ni-Cr-Ti alloy in the case of a Ni$_3$Ti phase. Thus, the general increase in the oxidation rate of a Ni-Cr-Ti alloy with temperature, beginning at 3.44%, may be explained by the increase in the Ni$_3$Ti phase in the alloy. The considerable reduction in the oxidation rate of a Ni-Cr-Ti alloy containing 0.68% Ti may be attributed to small additions of Ti (up to 2%), as shown in works $\underline{/108, 109/}$, which increases the bond energy between the atoms of this alloy. In this connection, the energy for the transfer of Cr, Ti and Ni ions from the alloy lattice to the oxide lattice will be greater than the energy for their transfer from a Ni-Cr lattice without Ti. Thus, in those cases when a Ti additive forms a solid solution, it somewhat lowers the oxidation rate of a Ni-Cr-Ti alloy for the above-mentioned reason. If Ti is contained in an alloy in such concentrations that the formation of large amounts of Ni$_3$Ti is possible, it increases the oxidation rate of a Ni-Cr-Ti alloy (in the authors' experiment, with 9.76% Ti at 1,000°).

The inter-crystallite corrosion discovered by the authors (see Figure 25) may also be explained by the formation of a Ni$_3$Ti phase along the grain boundary.

In conclusion, let us mention that, in agreement with the data of $\underline{/106/}$, that we have noticed a greater diffusive motion of Ti ions than of Cr ions, although their ionic radii (Cr^{3+} = 0.64 Å and Ti^{4+} = 0.64 Å) are the same.

Other alloying elements, just as Ti and Al, have a dual effect on Ni-Cr alloys. Also, metals such as niobium, tantalum,

molybdenum and tungsten increase the thermal stability of this alloy [116, 117] but lower its heat-resistant properties. The thermodynamic activities of these alloying elements in the alloy are very low, and their atoms exhibit low mobility. The diffusion coefficients of base metals, Ni and Cr, decrease in alloys containing Mo, W, Ta and Nb. All of these facts attest to the increased bond energy between the atoms in the lattices of alloys with additives of these metals. Energies for the transfer of ions of Cr, Ni and other components from the alloy lattice to the lattice of crystals of the oxide film will also be higher than in the case of nichrome without additives of these metals. Therefore, additives of Mo, W, Ta and Nb will decrease the general number of ions of alloy components reaching the alloy-coating boundary.

However, the oxidation process may be accomplished by other means than the diffusion of metal ions through the oxide film. For a number of metals, including Mo, W, Ta and Nb, the process takes place due to the diffusion of oxygen through the oxide film. Since oxide crystals of Ta, Nb, Mo and W occur in the coating along with crystals of oxides NiO, Cr_2O_3 and $NiCr_2O_4$, the oxide film loses its protective properties. An actual increase in the oxidation rate of Ni-Cr alloys with additives of Ta, Nb, Mo and W is observed at temperatures over $1,000^\circ$ and at a concentration of over 5% of these elements. The addition of tungsten, and especially over 5% of molybdenum, will lower the thermal stability of Ni-Cr alloys due to the high volatility of MoO_3 (beginning at 300°) and WO_3 (at $1,000^\circ$, especially in the presence of water vapor). The oxides Ta_2O_5 and Nb_2O_5 do not form stable chemical compounds with oxides NiO and Cr_2O_3 in the temperature range of $1,000$-$1,200^\circ$. In the course of time at this temperature interval a sufficient amount of Ta and Nb or Mo and W will accumulate to result in the formation of their oxide crystals. Vaporizing oxides MoO_3 and WO_3 create pores in the coating and thereby lower the thermal stability of Ni-Cr alloys considerably. Oxides Nb_2O_5 and Ta_2O_5, having high molecular weights, create high stresses in the coating, which results in the formation of fissures, and the coating begins to crumble from the alloy.

Thus, oxides of these alloying metals increase the oxidation rate of Ni-Cr alloys, not only because oxygen diffuses through their lattices, but also because they create pores and fissures in the coating.

In small amounts (up to 2%), when individual oxide phases of MoO_3, WO_3, Nb_2O_5, and Ta_2O_5 are not formed in the coating, this group of metals lowers the oxidation rate of nickel- and chromium-base alloys or does not affect its magnitude. The addition of 0.05-0.5% at. wt. of B to Ni-Cr alloys greatly increases their heat-resistant properties; and at $1,000^\circ$, either improves corrosion resistance or has little effect on it (this is determined by the

presence of other alloying elements). Increased thermal stability of alloys, probably, is connected with the formation of borides of some alloy components (for example, borides of chromium) along the grain boundary. At 1,000-1,100°, the thermal stability of alloys drops sharply, in which case, the weight of the samples is reduced after a period of time (about 20 hours) from the beginning of heating. The lowered stability and weight lost from the samples may be explained by the fact that, with increase in temperature, a sufficient amount of B ions penetrate the coating to effect the formation of crystallites of an oxide phase, B_2O_3. Since this oxide of boron melts at 450°, it does not form stable compounds with oxides NiO and Cr_2O_3 in the temperature interval of 1,000-1,200° and undergoes marked vaporization at these temperatures. Thus, an oxide film on alloys containing B will be porous, although its chemical composition remains basically the same as that of an alloy without boron. Electronograms /electron diffraction patterns/ of samples of such alloys show diffraction lines belonging mainly to spinel $NiCr_2O_4$. The high weight loss from the samples may be due to vaporization of the oxide phase B_2O_3, or due to the vaporization of MoO_3 or WO_3 if the metals of these oxides are contained in the alloy along with B. Those parts of the surface occupied by the liquid phase of B_2O_3 will not create means for the penetration of oxygen to the alloy-coating boundary or MoO_3 and WO_3 vapors to the coating--gaseous-medium boundary.

The high rate of oxidation of Ni-Cr alloys alloyed with vanadium is mainly connection with the low melting point of vanadium pentoxide V_2O_5 (670°), and also, with the fact that this oxide, like B_2O_3, does not form stable compounds with NiO and Cr_2O_3 at 700-1,000°.

It is most difficult at present to explain the marked influence on the thermal stability properties of Ni-Cr alloys shown by small amounts (up to 0.5%) of such additives as the rare earths (mainly lanthanum), calcium, and thorium. Up to the present, the location of these elements in a coating has not been experimentally determined, and in which form they are found in the body of an alloy has not been established. Therefore, on the basis of existing experimental data and by analogy with the nature of the influence of other elements on the properties of an alloy, it is possible to express only a conjectural evaluation of the effect of lanthanum, calcium and thorium on the thermostability of Ni-Cr alloys.

However, one could hardly expect an essential difference in the mechanism of the influence of the latter alloying elements with respect to those reviewed earlier. One might suppose that their influence will be analogous to the mechanism of the influence of Al and Si. Just as Al_2O_3 and SiO_2, oxides of La, Ce, Ca and Th have a high heat of formation (see Table 16), accumulate at the alloy-coating boundary as thin films, and retard the diffusion of ions of the base components of an alloy and atoms of oxygen.

Oxides of these elements easily form chemical compounds with the oxides NiO, Cr_2O_3, Al_2O_3, TiO_2, and others. Since the melting points and heats of formation of the oxides La_2O_3, CeO_2, CaO and ThO_2 are higher than those of NiO and Cr_2O_3, then the bond energies in lattices of solid_solutions or compounds of oxides of the first and second groups /of the periodic table/ will exceed the bond energies in the lattices of NiO and Cr_2O_3. In this connection, the decomposition temperature of oxide compounds of NiO and Cr_2O_3 alloyed with CaO, La_2O_3 and other oxides, is high in comparison with the decomposition temperature of $NiCr_2O_4$. In this case, the vaporization rate of the oxide Cr_2O_3 from the film during the decomposition of spinel $NiCr_2O_4$ decreases considerably, which occurs at 1,100-1,200° /90/, because the Cr_2O_3 will be held in compounds of the type $CaCr_2O_4$, $LaCr_2O_3$ and $CeCrO_3$. The positive effect on the corrosion stability of Ni-Cr alloys containing rare earths alloyed with Al and Si may also be explained by the fact that compounds with higher thermostability than spinels $NiAl_2O_4$, $NiCr_2O_4$ (or their solid solutions) are formed when oxides CaO, La_2O_3 and CeO_2 combine with oxides SiO_2 and Al_2O_3.

Thus, oxides of the alloying elements La, Ce, Ca and Th will increase the protective properties of oxide films consisting of $NiCr_2O_4$, $NiAl_2O_4$ and other compounds, and lengthen the service life of Ni-Cr alloys.

The predicted mechanism of increasing the corrosion resistance of Ni-Cr alloys at high temperatures by adding small amounts of rare earths (mainly La, Ce, Ca and Th) has not been proven by the authors at present.

So, the authors have reviewed the experimental results of studies on the oxidation of Ni-Cr alloys and have attempted to qualitatively describe the oxidation mechanism of these alloys and the mechanism of the effect of various alloying elements on their oxidation rates. Along with kinetic data, the authors have utilized the thermodynamic characteristics (heat of formation, melting point and vaporization rate) of both the alloys themselves and their compounds, and also, the oxides.

From the foregoing material, the following main conclusion can be drawn as to the oxidizability of Ni-Cr alloys:

1. The oxidation process is carried out mainly by the diffusion of ions of alloy components, although at high temperatures (900-1,100°), oxygen diffusion is observed.

2. The compositions of coatings on alloys at high temperatures is determined by the thermodynamic activities of the alloy components, and also, by the heats of formation of the oxides.

3. As to the mechanism of the effect of all alloying components on the corrosion resistance of Ni-Cr alloys, the elements introduced to improve the physicochemical properties and, first of all, to increase thermostability, may be divided into two

groups. One of these groups, which includes Al in small amounts, Si (up to 2%), La, Ce, Ca, and Th (up to 0.3-0.5%), increases the thermostability of nickel- and chromium-base alloys.

The other group, including B, Mo, W, Nb, Ti and Re, may considerably lower the thermostability of these alloys when added in large amounts (over 5%, and for B, over 0.1%).

4. The most protective against gaseous corrosion are oxide films consisting of a single-phase chemical compound or a solid solution. For Ni-Cr alloys, such compounds include spinels $NiCr_2O_4$ and $NiAl_2O_4$ (upon addition of 4-7% Al) and their solid solutions.

5. The corrosion resistance of Ni-Cr alloys with and without additives of small amounts of B, Mo, W, Nb and other elements is considerably lowered at temperatures over $1,000°$, because spinel $NiCr_2O_4$, of which the coating on the alloy mainly consists, decomposes into NiO and Cr_2O_3 at $1,100-1,200°$, in which case, Cr_2O_3 undergoes marked vaporization at these temperatures.

6. The increased thermostability and service life of Ni-Cr alloys, containing Al, Ce, Th and rare earths, at $1,100-1,170°$, is due to the alloying action of oxides of these elements on the oxides NiO and Cr_2O_3, with which the former form chemical compounds and thus prevent the formation of free chromium oxide /which undergoes marked vaporization at these temperatures, as stated above/.

One of the main shortcomings of studies of the oxidation mechanism of both Ni-Cr and other alloys is that the experimental results of these studies are mainly obtained using filiform and/or sheet samples in the unloaded /i.e., unstressed/ state.

However, the authors' electronographic /electron diffraction/ studies of the structure and composition of oxide films on the vanes /turbine blades/ of jet engines showed that their phase and chemical composition were the same as in unloaded samples. The kinetics of the oxidation processes of loaded samples (especially during continuous stresses) will, apparently, take place considerably faster than that of unloaded samples, because the system in the first case possesses more free energy than in the second case. Also, the elasticity of the coating and its strength of adhesion to the alloy surface will have great effect on the kinetics of the process.

Studies of the oxidation processes of alloys are important not only for understanding the mechanism of chemical reactions in the solid phase but also for obtaining practically valuable characteristics on the thermostability of alloys. Data on the composition of oxide films permit the determination of which of the alloying elements is transferred from the alloy into the coating. In particular, the impoverishment of elements from the surface of working parts may be determined from the compositions of oxide films. Probably, one of the reasons for the formation of surface cracks is the impoverishment of alloying elements in the surface layers of parts.

To combat these phenomena and to increase corrosion resistance, it is beneficial to impregnate the surfaces of parts made from Ni-Cr alloy with those elements having high thermodynamic activity in the alloy, and whose oxides give good protective surface films.

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FIGURE APPENDIX
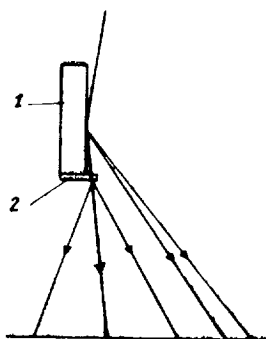
Figure 1. Diagram of the path of the electron beam upon photographing 1, a bulk sample and 2, a thin aluminum film.

Figure 2. Electron diffraction pattern obtained by simultaneously photographing the oxide film on a bulk sample and a thin aluminum film.

F
5
9
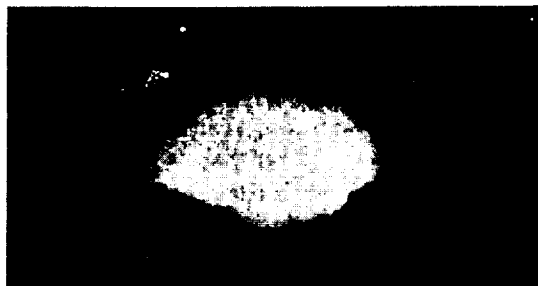
a

b

c

Figure 3. Electron diffraction patterns: a and b -- surface layer
of a coating on Ni samples oxidized 11 hours at 800°;
c -- internal layers of a coating on the same sample.
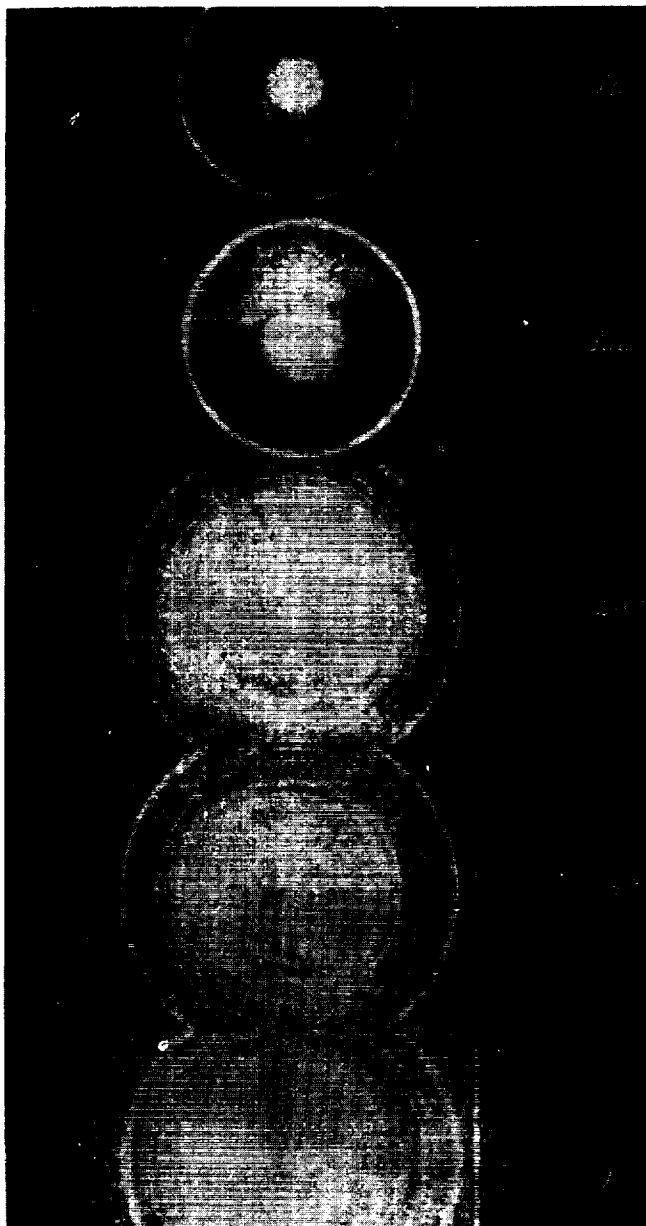
Figure 4. Electron diffraction patterns of thin films on Cr oxidized in air at temperatures from 20 to 1,000°.
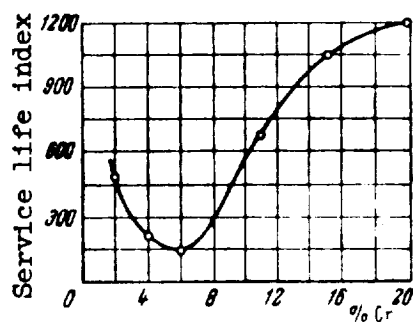
Figure 5. Service life of Ni-Cr alloys in dependence on Cr content /18/.
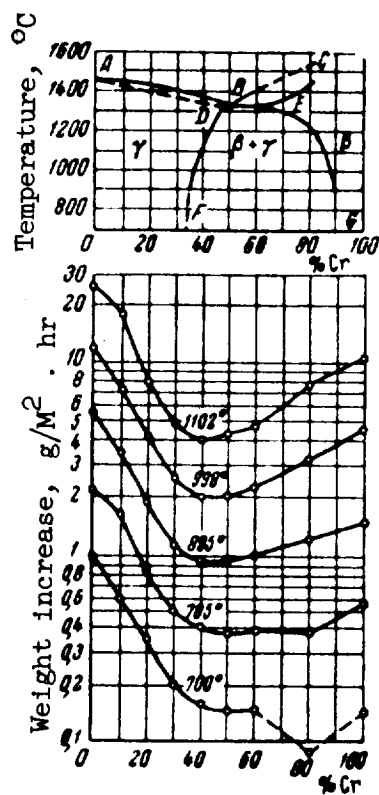
Figure 6. Dependence of the thermostability of Ni-Cr alloys on their composition and composition diagrams of Ni-Cr alloys.
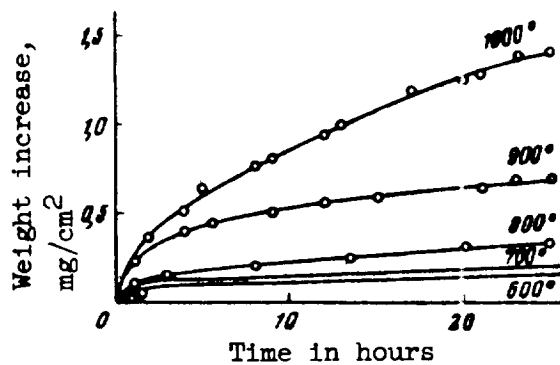
Figure 7. Weight increase - time curves for 80% Ni + 20% Cr alloys at 600-1,000°.
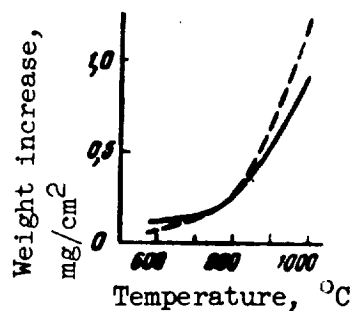
Figure 8. Weight increases of Cr samples and of 80% Ni + 20% Cr alloy samples after 11 hours: --- Cr, ___ alloy.
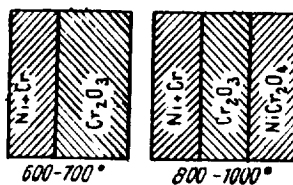
Figure 9. Structural diagram of the film on an 80% Ni + 20% Cr alloy.

Figure 10. Cross section of an 80% Ni + 20% Cr alloy sample oxidized over a period of 25 hours at 1,000°.
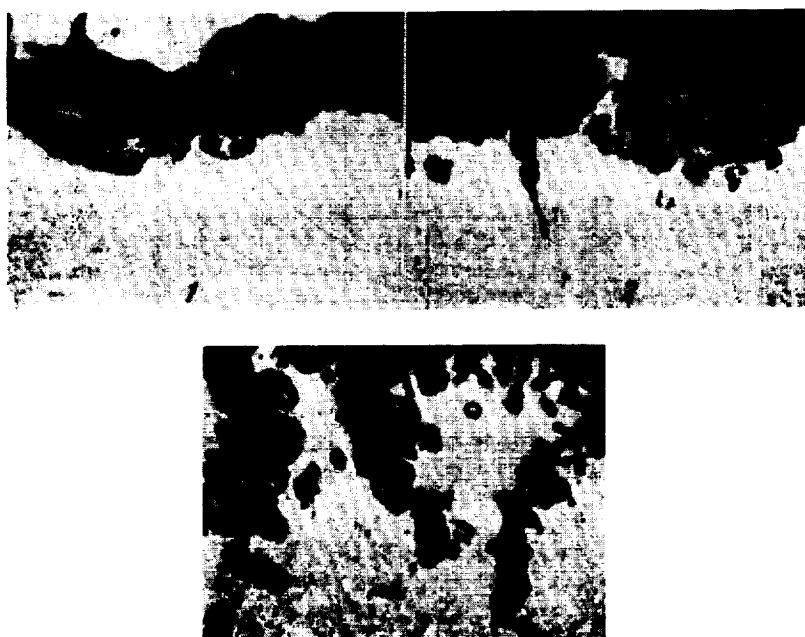
Figure 11. Cross sections of samples subjected to 1,529 alternate heating and cooling cycles at 1,176°: 1 -- alloy Nr 13246; 2 -- alloy Nr 12246; 3 -- alloy Nr 12046. x 750 /87/.
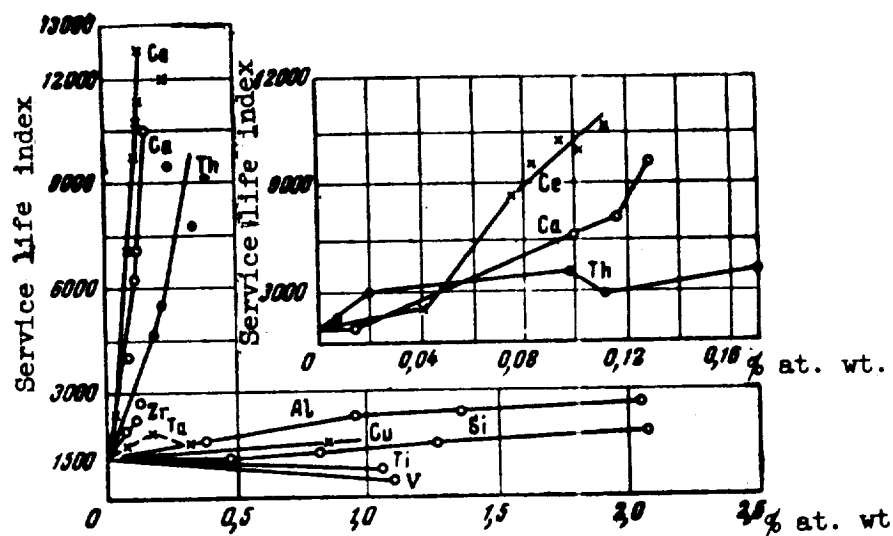
Figure 12. The effect of different additives on the service life
of an 80% Ni + 20% Cr alloy /18/.
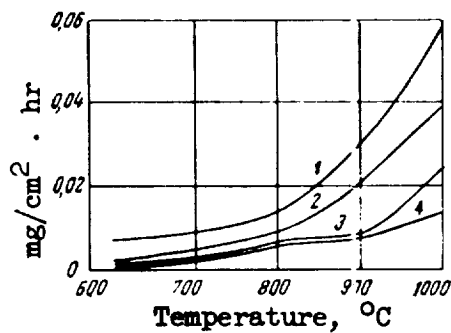
Figure 13. Dependence of oxidation rate on temperature for Ni-Cr
alloys: 1 -- 0% Al; 2 -- 1% Al; 3 -- 4.18% Al; 4 --
7.22% Al.
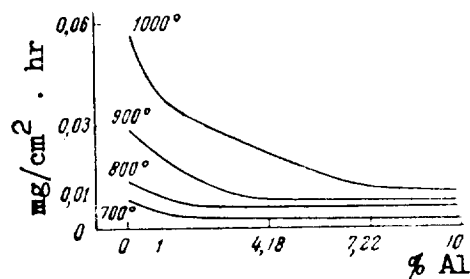
Figure 14. Dependency of oxidation rate on the composition of Ni-Cr alloys.
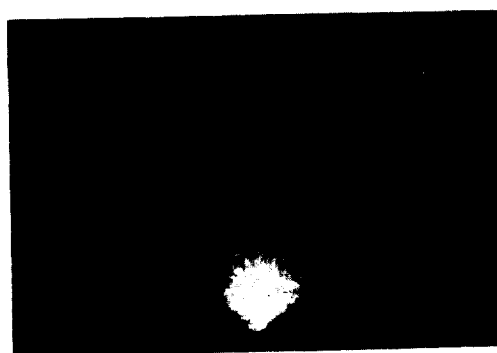
Figure 15. Electron diffraction pattern of the coating on a Ni-Cr alloy, consisting of a spinel-type oxide with [lattice] constant a = 8.30 Å.
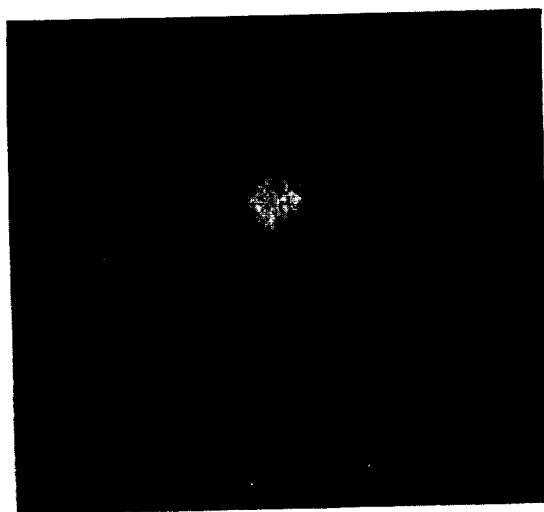
Figure 16. Electron diffraction pattern of a thin film of oxide $NiCr_2O_4$.

Figure 17. Electron diffraction pattern of the coating on a Ni-Cr-7.22% Al alloy, consisting of a spinel-type oxide with constant a = 7.9 Å.
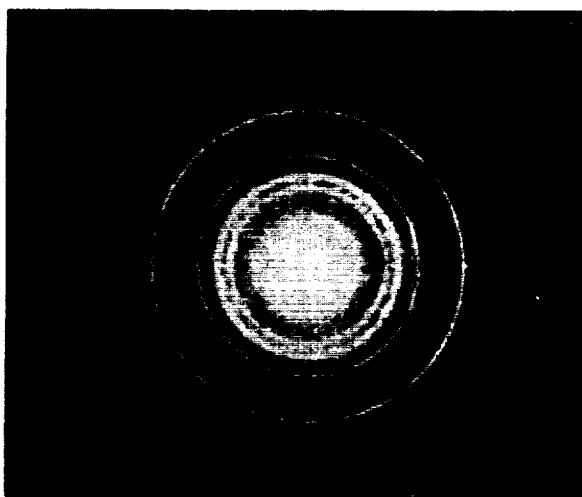
Figure 18. Electron diffraction pattern of a thin film of oxide $\gamma = Al_2O_3$.
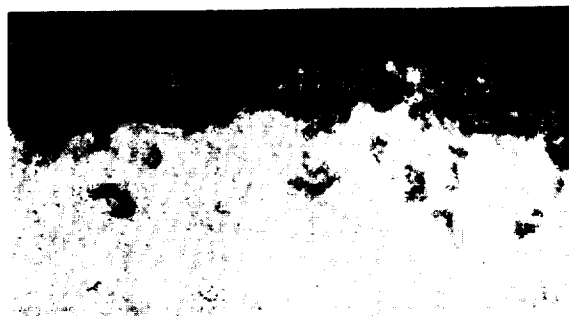
Figure 19. Cross section of a Ni-Cr-1% Al alloy sample oxidized over a period of 25 hours at 1,000°. x 800.
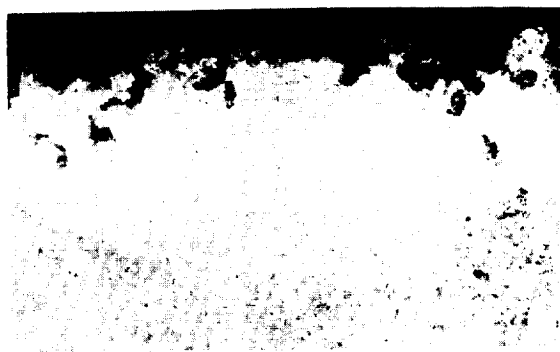
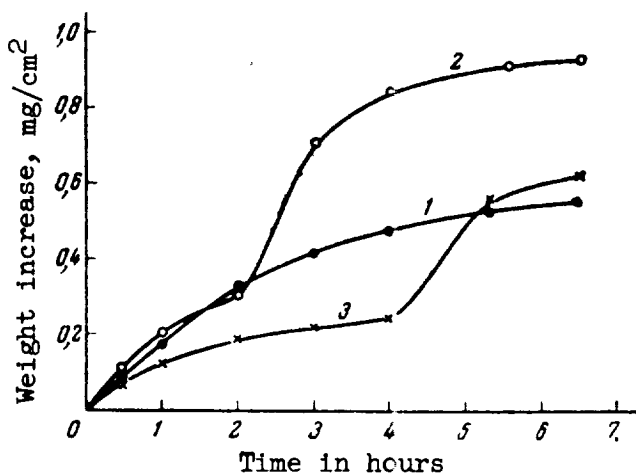Figure 20. Cross section of a Ni-Cr-4.18% Al alloy sample oxidized over a period of 25 hours at 1,000°. x 800.

Figure 21. Cross section of a Ni-Cr-7.22% Al alloy sample oxidized over a period of 25 hours at 1,000°. x 800.

Figure 22. Weight increase - time curves for Ni-Cr-Al alloys at
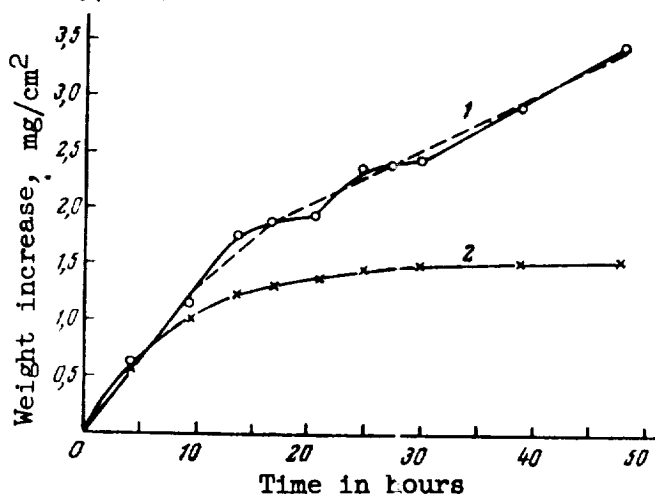900°: 1 -- 5% Nb; 2 -- 2.5% Nb; 3 -- 10% Nb.

Figure 23. Weight increase - time curves for Ni-Cr-Al-Nb alloys
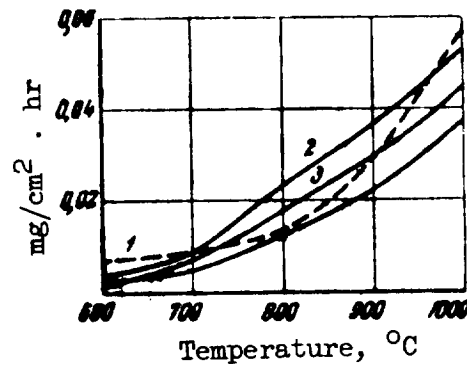at 1,000°: 1 -- 5% Nb; 2 -- 2.5% Nb.

Figure 24. Dependence of the oxidation rate of Ni-Cr-Ti alloys on temperature: 1 -- 0% Ti; 2 -- 3.44% Ti; 3 -- 5.88% Ti; 4 -- 0.68% Ti.

Figure 25. Cross section of a Ni-Cr-5.88% Ti alloy sample oxidized over a period of 25 hours at 1,000°. x 600.
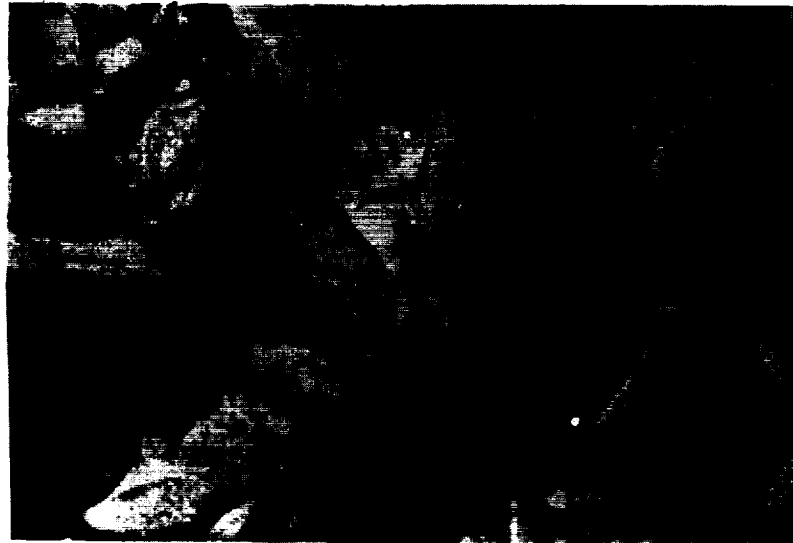
Figure 26. Electron microphotograph of the coating on an alloy sample containing 0.5% B, oxidized over a period of 100 hours at 900°. x 35,000.

Figure 27. Electron microphotograph of the coating on an alloy sample containing 0.007% B, oxidized over a period of 100 hours at 900°. x 35,000.

Figure 28. Electron microphotograph of the coating on an alloy sample containing 0.5% B, oxidized over a period of 100 hours at 1,030°. x 25,000.

Figure 29. Electron microphotograph of the coating on an alloy sample containing 0.007% B, oxidized over a period of 100 hours at 1,030°. x 25,000.

NiO	NiO	NiCr$_2$O$_4$	NiCr$_2$O$_4$	Cr$_2$O$_3$	Cr$_2$O$_3$
1	2	3	4	5	6

Figure 30. Arrangement of the oxide samples in the experiments of Hauffe and Pschera /74/.

104

mg/cm²

ZnO

Cr₂O₃

NiOCr₂O₃

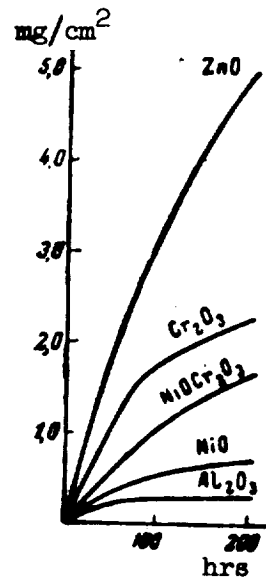NiO

AL₂O₃

hrs

Figure 31. Vaporization rate of oxides in air at 1,100° /74/.

400°   500°   600-700°
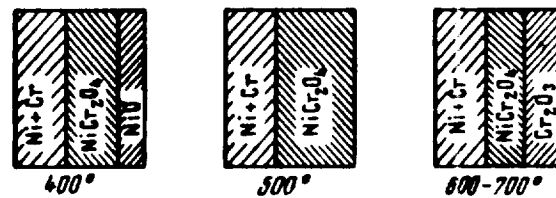
Figure 32. Predicted structural make-up of a coating /oxide --
on a Ni-Cr alloy/ according to P. D. Dankov /40/.
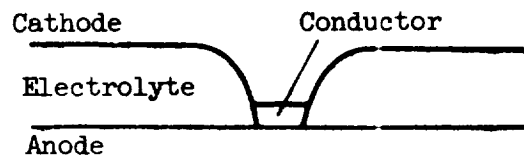

Cathode   Conductor

Electrolyte

Anode

Figure 33. Scheme of oxide film growth according to Frantsevich
/104/.